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*Manson James Bradley.*

*A Study of Decomposition Processes  
Applicable to Certain Products of Coal Carbonization.*



A STUDY OF DECOMPOSITION PROCESSES  
APPLICABLE TO CERTAIN PRODUCTS  
OF COAL CARBONIZATION

BY

MANSON JAMES BRADLEY  
A. B. McMaster University, 1915  
A. M. McMaster University, 1915

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THESIS

Submitted in Partial Fulfillment of the Requirements for the

Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

IN

THE GRADUATE SCHOOL

OF THE

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Manson James Bradley  
ENTITLED "A Study of Decomposition Processes Applicable  
to Certain Products of Coal Carbonization."


BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
THE DEGREE OF Doctor of Philosophy in Chemistry

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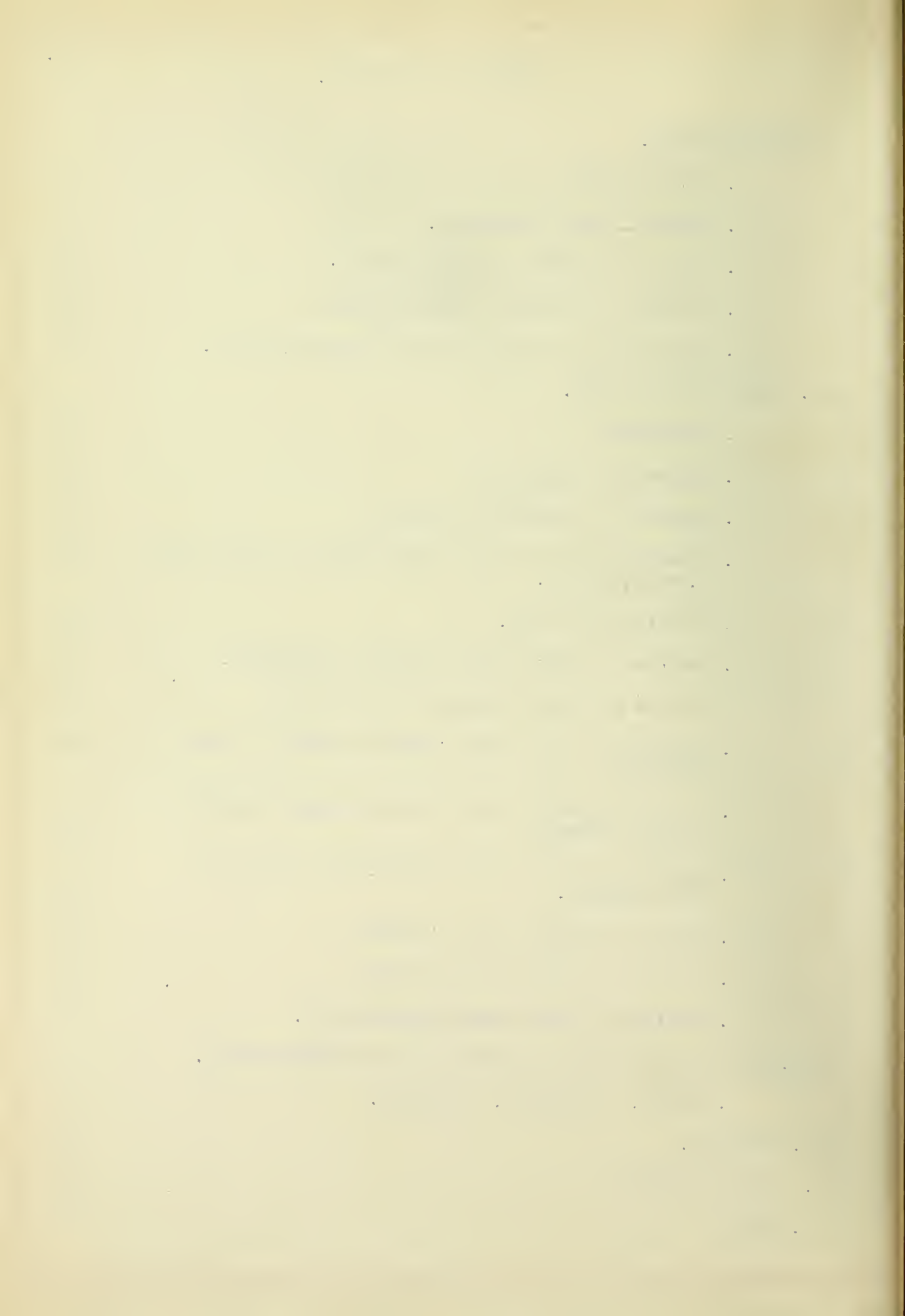
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A STUDY OF DECOMPOSITION PROCESSES APPLICABLE TO  
CERTAIN PRODUCTS OF COAL CARBONIZATION.

1. INTRODUCTION.

I. PRELIMINARY.

In undertaking a complex investigation such as that of the reactions occurring during the decomposition of the products of coal carbonization, there are two principal procedures to follow. One might take the crude material in all its complexity, decompose it under diversified conditions, and, by the careful examination of accurately recorded results, endeavor to arrive at definite conclusions, the validity of which could be established by further observation, or by modifying details in the direction indicated. This is the intelligent and progressive practice followed by industrial concerns. Alternatively, one might try to arrive at a better understanding of the intricate complex by a preliminary study of single constituents, determining, for example, the mode of formation and decomposition of some one constituent of coal carbonization under a variety of conditions, including, as of primary importance, those conditions to which it would be subjected in carbonizing practice. This method is particularly suited to the laboratory and is the principle underlying the following investigation. Even the study of the decomposition of a single constituent becomes very complex when we take into consideration, the factors that influence equilibrium in any gaseous chemical reaction. Among these factors, temperature, pressure, concentration or mass action,





duration of time of contact or reaction, and contact surfaces are of prime importance. Several of these factors, such as temperature control, may be sub-divided into a number of problems, each of which may be very difficult of solution, especially if it is desired to construct large scale apparatus for the commercial production of these decomposition products.

## 2. GENERAL CONSIDERATIONS.

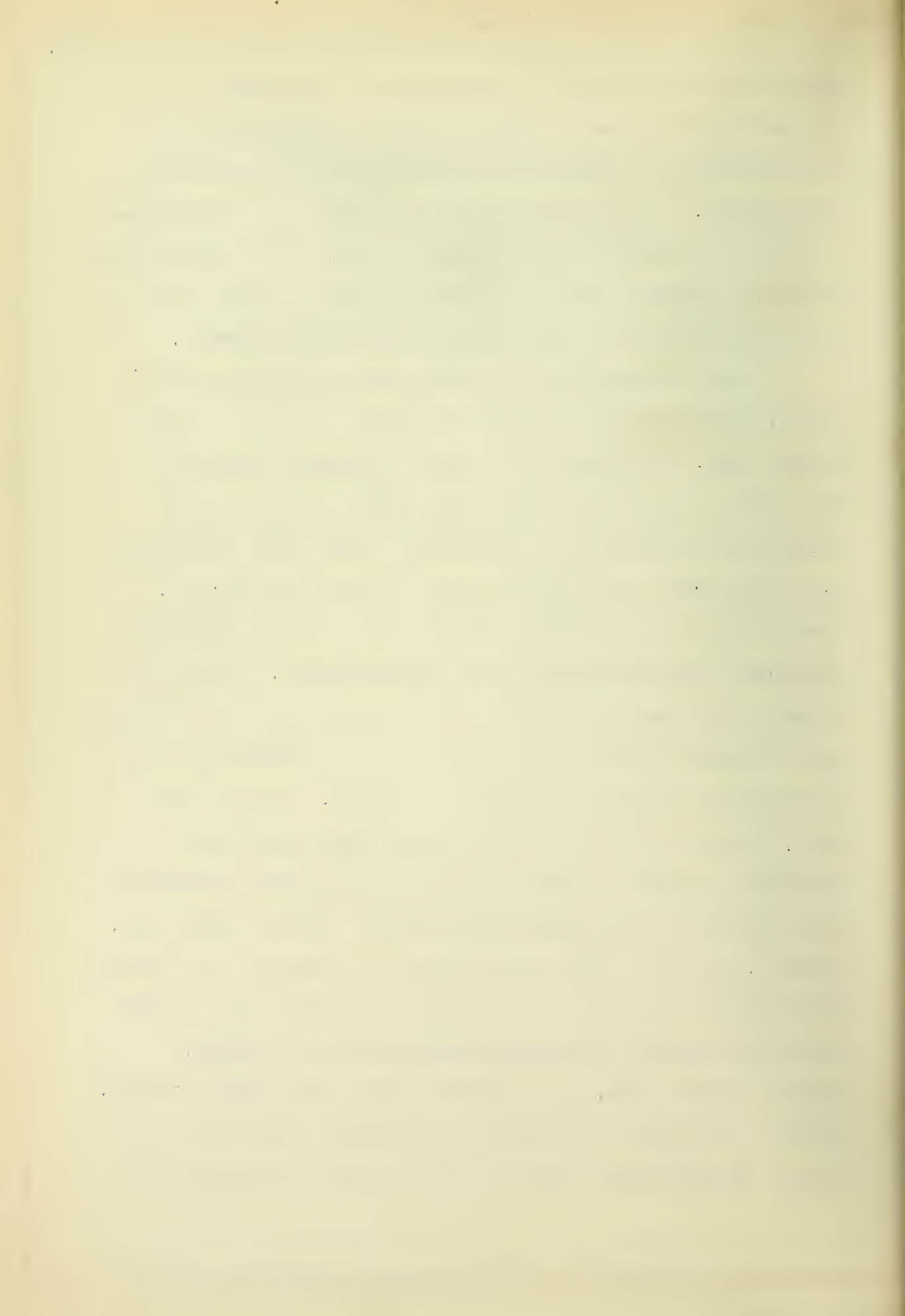
True equilibrium, that state in which reactions proceed equally in each direction, is seldom attained in any hydrocarbon decomposition. Under constant pressure there is a definite proportion of the individual constituents for each temperature; under constant temperature there is a definite proportion between the reacting constituents for each pressure, even if the numerical value of the equilibrium constant is a function only of temperature. Heat can supply the energy necessary to change an existing state of chemical inertia and cause reaction between the various molecular formations but too high a temperature, during an extended period of time, permits the hydrocarbon to decompose into carbon and permanent gases. The farther the system is from stable equilibrium the greater the tendency for reaction to take place. Changing the temperature may bring the system nearer to the desired equilibrium point. No single equilibrium, however, can be considered by itself because all the constituents must also be in equilibrium, or a system of





equilibria between all the components of the system. In an unbalanced system of gases there is a tendency for an equilibrium to be established between all the components of that system. All the reactions that occur in a hydrocarbon process are interrelated and must be taken into consideration even if a single reaction or set of reactions may be extremely important as indicating a prevailing tendency.

The decomposition of hydrocarbons increases with rise in temperature and with the duration of time in the heated zone. Le Chatelier's theorem predicts that an increase in temperature will drive the reaction in the direction in which heat is absorbed. Thus heavy molecules are less stable than lighter ones of similar structure. Indications of the effect of temperature on decomposition processes may be obtained from thermodynamics. Bertholet advanced a proposition which can be summarized as follows, - every chemical change gives rise to those substances that occasion the greatest development of heat. If this were true, the problem of obtaining temperature indications would be as simple as that of obtaining pressure indications for reactions proceeding to equilibrium. That proposition, however, is only a first approximation, because in all chemical reactions there is additional molecular energy, whereas the proposition mentioned assumes the free energy, termed maximum work, to be equal to the total energy change. Nernst has pointed out that this statement holds true only at the absolute zero; that is, the entropy of liquids and



solids at absolute zero of temperature equals zero. The temperature most favorable for the production of the largest quantity of any particular aromatic hydrocarbon is quite different from the optimum temperature for the formation of a higher or lower homologue. The temperature best suited to the formation of naphthalene is quite different from that required in the formation of benzene and as we approach or depart from this optimum temperature the yield of the desired hydrocarbon increase or decrease proportionately.

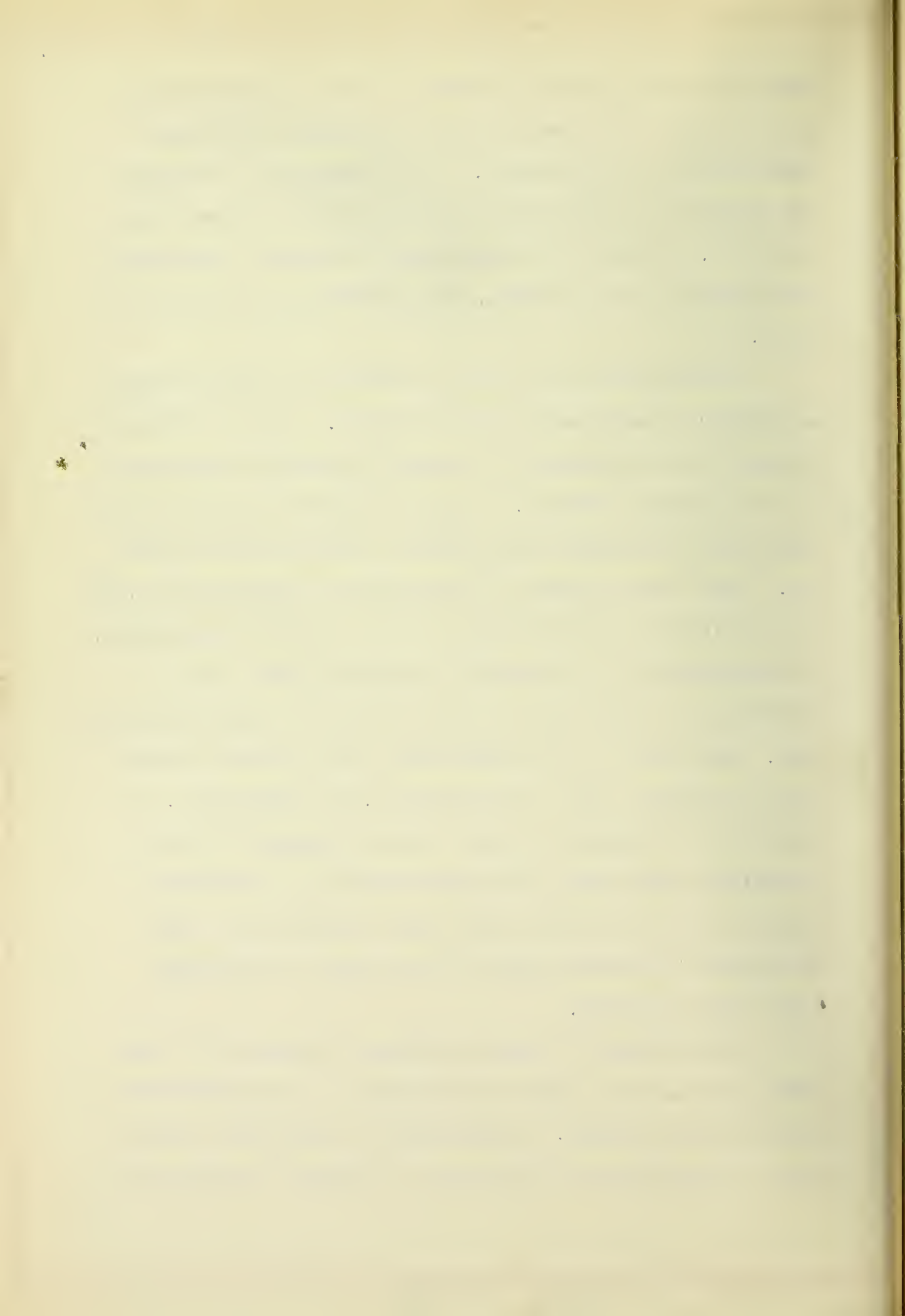
When considering the effect of pressure on a gaseous system similar difficulties are encountered as in the case of temperature. The application of Le Chatelier's principle shows that pressure favors any reaction resulting in decrease in volume and opposes any reaction that is accompanied by an increase in volume. Stated in another way, diminished pressure, increases decomposition of hydrocarbons or increases the formation of gas, while increase in pressure decreases decomposition or tends to form liquid and solid compounds. It appears possible, therefore, to obtain indications of the effect of pressure by simply writing the chemical equation and summing up the volume changes. However, it must be remembered that pressure produces a change in the concentration of the reacting substances, which may produce a marked change in the reaction of constituents in the system. According to the law of mass action, the velocity of a chemical



reaction, at any small intervals of time, is proportional to the amount or concentration of substance undergoing transformation at that time. So an increase in pressure may promote decomposition or chemical change rather than retard it, because of the additional variables unavoidably introduced at the same time, thus defeating the result desired.

The duration of time of reaction is a very important factor in any gaseous decomposition. It is intimately related to the temperature, pressure, gaseous constituents and end products desired. Organic reactions seldom come to equilibrium instantly but required a definite time interval. This time interval, in hydrocarbon decompositions, can be controlled in several ways, the two easiest manipulated, are lengthening or shortening the heated zone, or by increasing or decreasing the rate of feed through the heated area. Obviously a high temperature will require a lesser time of contact, than a relatively lower temperature. A slow rate of feed and a relatively low temperature will accomplish practically the same results as a relatively faster rate of feed at a much higher temperature, with the single difference that more time will be necessary for a given quantity.

The effect of contact surface is perhaps the most indefinite and most important variable in any hydrocarbon decomposition process. The phenomena of catalytic acceleration or retardation of physical or chemical processes are





so common as to defy systematic classification, since such a complete system would necessarily include all possible types of reactions, both homogeneous and heterogeneous. Ostwald's often quoted statement, - "There is probably no kind of chemical reaction which cannot be influenced catalytically and there is no substance, element, or compound which cannot act as a catalyser", - indicates the comprehensive susceptibility of catalysis.

Many theories have been propounded to explain the mechanism of catalytic reactions. Faraday's concept of catalytic activity being due to selective adsorption phenomena was advanced by J.J. Thomson<sup>1</sup> coupled with Laplace's theory of capillarity. Bancroft's<sup>2</sup> latest statements, that selective adsorption permits of different reactions being accomplished with the aid of different catalytic materials, emphasis two important details, namely, catalysts tend to produce the system which they adsorb most strongly and the compound or adsorptive layer may be regarded as a solvent and hence may exert an influence on the final equilibrium.

Sabatier<sup>3</sup>, after many years spent in investigation with nickel catalysts in hydrogenation processes, came to the conclusion, that the formation of an intermediate compound with the catalyst and reacting substance, was the best explanation for this extraordinary activity. In many





organic catalytic processes, such as the formation of ether, Friedel-Crafts reaction, Grignard reagent and many others, the intermediate compound can be isolated. An extremely interesting modification of this theory was advanced by Armstrong.<sup>4</sup> To him, chemical combination is reversed electrolysis, and the function of the catalyst is to form a circuit containing at least three distinct terms or components analogous to a closed voltaic circuit. By this means the catalytic agent collects into one system the various elements necessary for a particular chemical change, and may be said to form molecular complexes with the reactants.

A recent theory of catalysis, somewhat of an electrochemical nature, has been advanced by Langmuir<sup>5</sup> and Harkins.<sup>6</sup> According to Langmuir, the adsorbed film, which is bound to the adsorbing surface by chemical forces, namely, the primary or secondary valencies, should be only one molecule thick and in this layer there exists an orientation of the molecules. He has developed this general theory of adsorption to the particular case of the adsorption of gases by plane, solid surfaces, and gives the results of a series of experiments on the adsorption of various gases by sheet platinum, glass, and mica at low pressures and various temperatures. This theory takes into account directive as well as selective adsorption, thus bridging the gulf between the theory of the intermediate compounds and the purely adsorption idea, since the postulate of directive force necessarily



assumes some form of chemical union between the contact surface and the molecules of the surrounding medium. These theories are discussed by E. Rideal and S. Taylor in their recent text, "Catalysis in theory and practice".

### 3. SCOPE OF PREVIOUS INVESTIGATIONS.

In the following résumé on pyrogenetic reactions of aromatic hydrocarbons only those investigations that seem most important in connection with the present problem are mentioned. Much work has been done on the problem of thermal reactions of aromatic hydrocarbons, but, on account of the many variables encountered, no systematic study of these reactions have appeared in the literature.

The historical researches of Bertholet<sup>7</sup> have furnished a foundation for succeeding investigations with pure aromatic hydrocarbons. His work was comprehensive and the results obtained very valuable. He passed the vapors of pure hydrocarbons through "red hot tubes" and obtained the general results as follows: from benzene he obtained diphenyl, chrysene and resin; from toluene he recovered benzene, toluene, naphthalene, anthracene and chrysene; from xylene he collected benzene, toluene, xylene, naphthalene, and anthracene; while anthracene yielded benzene and chrysene. From the mixed vapors of naphthalene and benzene he obtained anthracene and from benzene and ethylene he recovered anthracene and diphenyl. No yields of products are reported in these publications and the temperature designated by the term "red-hot" is very indefinite.



Recently, Zanetti<sup>8</sup> and Kendall have studied the pyrogenetic production of anthracene from benzene and ethylene in a quantitative manner and at various temperatures. They bubbled the ethylene through the benzene and passed the vapors through a heated quartz tube. Their best yield, (0.675% from the total benzene used), was obtained at 925° C and at atmospheric pressure. At this temperature the sum of the yields of diphenyl and carbon is a minimum and above it the formation of carbon occurs very rapidly.

In some previous experiments conducted by Zanetti and Egloff<sup>9</sup>, on the thermal decomposition of benzene with catalysers, they found that benzene could be decomposed to diphenyl at a temperature as low as 500° C, but did not believe that copper iron or nickel gauze inserted in the craking tube, catalysed the reaction. However, iron and nickel did seem to catalyse the reaction to carbon and hydrogen.

Some valuable information indicating the direction of reactions in the thermal decomposition of hydrocarbon vapors was obtained by Ferko<sup>10</sup> by passing the vapors through a "red hot" iron tube. The temperature he used was very indefinited and the pressure is not mentioned, no doubt, the results given are at atmospheric pressure. From benzene and ethylene he recovered benzene, styrolene, diphenyl, phenanthrene and anthracene; from toluene he obtained benzene and anthracene; while from toluene and ethylene he iden-



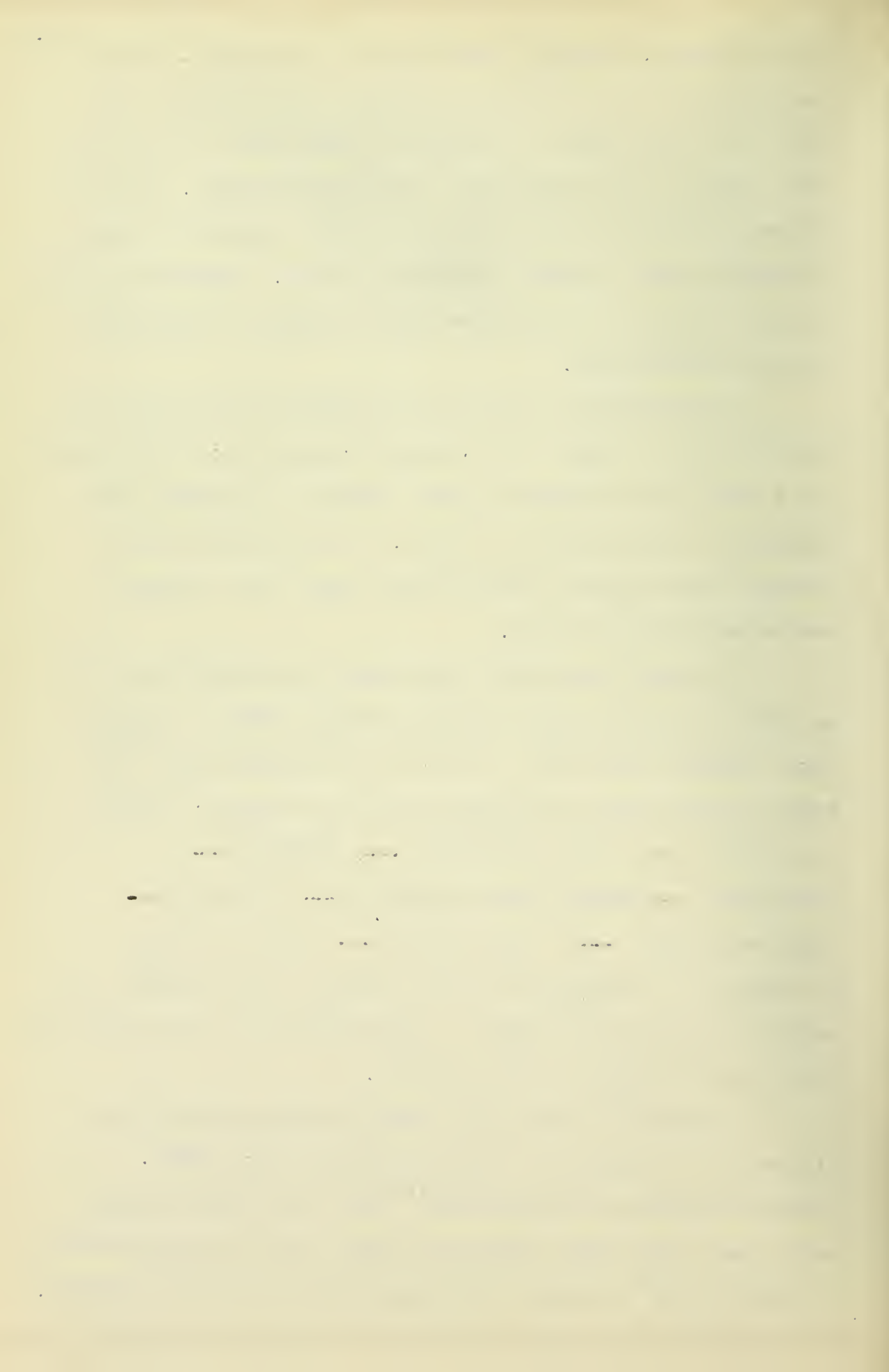


tified benzene, toluene, styrolyene and anthracene. These results show that no reaction products were obtained that were not in the order of decrease of saturation or of molecular weight if the saturation remained unchanged. That is, benzene yielded no toluene nor any other compound of equal saturation and of greater molecular weight. Naphthalene gave neither benzene or toluene but small amounts of dinaphthalene and phenanthrene.

From Haber's<sup>11</sup> work on the thermal decomposition of hydrocarbons he found that benzene decomposes with difficulty above  $900^{\circ}\text{C}$  and although it goes readily to diphenyl and hydrogen no naphthalene is formed. He concludes that in aromatic hydrocarbons decomposition takes place between carbon and hydrogen atoms.

In some qualitative experiments by McKee<sup>12</sup> in which he passed benzene vapors through a copper tube at temperatures ranging from  $450^{\circ}\text{C}$  to  $785^{\circ}\text{C}$ , he concluded that the order of hydrocarbon decomposition is as follows: higher paraffines  $\rightarrow$  lower paraffins  $\rightarrow$  Olefins  $\rightarrow$  acetylenes  $\rightarrow$  benzene and homologues  $\rightarrow$  diphenyl  $\rightarrow$  naphthalene, etc.  $\rightarrow$  tarry matter  $\rightarrow$  carbon and gas. No analysis or separation of the products was attempted, he merely determined the degree of decomposition by the change in the specific gravity of the product.

Ipatieff<sup>13</sup> found that benzene decomposed with the liberation of hydrogen, forming diphenyl above  $600^{\circ}\text{C}$ . Ostromisslenske and Burshanadse<sup>14</sup> found that when benzene vapor was passed over nickel or nickel oxide at temperatures of  $600^{\circ}$  to  $750^{\circ}\text{C}$ , carbon and hydrogen were the main products.





Smith and Lewcock<sup>15</sup> passed benzene vapors through an iron tube containing different catalysers such as barium oxide and coke, and found that diphenyl was not formed below 670°C. but at 800°C. they obtained a 25% yield of diphenyl. They could not reverse the reaction, and noticed that the yield of diphenyl increased with the rate of feed, indicating that diphenyl was an intermediate, rather than an equilibrium product.

Rittman, Button and Dean<sup>16</sup> in their pyrogenetic decomposition of aromatic hydrocarbons, in the vapor phase, passed benzene, toluene, xylene, naphthalene and anthracene through iron tubes at temperatures ranging from 650° to 800°C and from diminished pressure up to pressures of 18 atmospheres. They also came to the conclusion that the course of the reaction is in the direction of the decrease in the size of the molecule, when the degree of saturation remains unchanged. Dehydrogenation, either with an increase or decrease in the size of the molecule, may occur but the reverse reactions are negligible.

Charlton<sup>17</sup> made three distillations of xylene at temperatures between 600°C and 700°C through an iron tube containing charcoal, also with charcoal impregnated with nickel, in the presence of superheated steam, to determine the relative yields of toluene and benzene. At 650°C. and atmospheric pressure, when using nickel charcoal catalyser,



the recovered benzene equalled 0.33%, and the toluene 0.40%, while the higher boiling fraction equalled 4.56% of the toluene used. Another experiment at the same temperature using the same catalyser but allowing the superheated steam to build the pressure up to 40 pounds per square inch, produced 0.958% benzene, 3.6% toluene and 9.12% higher boiling compounds. When running under 110 pounds pressure the yield of benzene increased to 1.45% but the other products became less.

It is interesting to note that at atmospheric and 40 pounds pressure no paraffine hydrocarbons were obtained but as high as 28.0% unsaturated aliphatics were found in the product. At 110 pounds pressure the unsaturated compounds were reduced 100% while 10.0% of paraffines were obtained. In the high boiling oils, monomethyl anthracene separated out but no naphthalene was found in any of these experiments.

In the researches of Cobb and Dufton,<sup>18</sup> on the thermal decomposition of pure aromatic substances, benzene, toluene, xylene, and cresol, were vaporized and passed through a silica tube containing coke at various temperatures, in the presence of hydrogen or nitrogen and the decomposition products collected and analysed. These results are the most important of any published along this line. They found that benzene could be stabilized at temperatures of 750°C by having the gaseous mixture consist of 93 per



cent hydrogen. Under low concentrations of hydrogen diphenyl was formed. They proved that the diphenyl formation was an equilibrium reaction by saturating hydrogen with diphenyl vapors at  $90^{\circ}\text{C}$  and passing the mixture through the tube at  $750^{\circ}$  and obtaining benzene. From toluene they recovered benzene, ditolyl and anthracene and from xylene they obtained benzene, toluene, diphenyl, and anthracene. These results are given on a quantitative basis together with much other valuable information.

#### 4. OUTLINE OF THE PRESENT INVESTIGATION.

The object of the present experimental work, broadly stated, was to determine the effect of various combinations of temperature, pressure, concentration, and contact surfaces on the course of decomposition reactions of aromatic hydrocarbons, in the vapor stage, and to determine, if possible, the most favorable conditions for the maximum yield of the various desired decomposition products, such as benzene, toluene or anthracene. In the extensive experimental work carried on in these laboratories on the coking of Illinois coals.<sup>19</sup> Utah coals, and many other varieties, it has been found possible to increase the quantity of tars and oils produced from two to four fold, by means of low temperature carbonization. The distillate obtained, in this manner, contains a large quantity of neutral, low boiling





aromatic oils, some of which, under normal commercial conditions, are considered of little importance in the industrial field. For instance, xylene in its present status, is a product scarcely worthy of recovering and purifying, yet by application of known methods of recovery, could be produced, under present conditions, in enormous quantities. This hydrocarbon, having a boiling point of  $137^{\circ}$  to  $141^{\circ}\text{C}$  has too low a vapor pressure for an efficient motor fuel, however, if by methods of pyrogenic decomposition, it can be converted into benzene, which has a boiling point of  $80^{\circ}\text{C}$ , its value as a motor fuel is greatly increased. If this decomposition can be accomplished, in yields, approaching anything like theoretical and in commercial quantities, the hydrogen and methane liberated ought to more than supply the heat energy required in the operation. Xylene can be decomposed with anthracene as an end product, but under existing methods the yield is small. If this decomposition could be made on a commercial scale and in yields sufficient to warrant its use, one of the main props in the synthetic dye industry would be assured. Ever since 1856 when Perkin produced the first alizarin dye from anthracene, the increase in production of this hydrocarbon has been eagerly sought. During the last few years it has been demonstrated how important the dye industry in this country has become.

In this investigation pure xylene was passed through an electrically heated furnace, at various temperatures,





different rates of feed, under various pressures, in the presence of such contact surfaces as iron oxides, reduced iron, copper, tin, molybdenum, chromium, Illuim, aluminium, nickel, cobalt, manganese, charcoal, pumice and refractory, the condensable compounds collected, weighed and analysed, also the gas was measured and analysed. Not only was the above variables tried out but the vapor condition inside the furnace was influenced by passing in at the same time as the hydrocarbon, air, superheated steam, carbon dioxide, carbon monoxide, hydrogen, nitrogen or ethylene.

#### 5. GROUPING OF RESULTS OF THE INVESTIGATION.

The facts established by this investigation may be briefly summarized as follows:

(1) Mixed xylenes were decomposed by heat and contact surfaces, under the stabilizing influence of hydrogen and methane, almost theoretically into benzene and methane. Sixty-nine percent of the original xylene was converted into crude benzene, which boiled below  $100^{\circ}\text{C}$ . This is approximately 94.0 percent of the possible theoretical.

(2) At slightly lower temperatures, under the same conditions of contact surfaces, but in a gaseous atmosphere in which ethylene greatly predominated, seventy-seven percent of the mixed xylenes were built up into higher boiling compounds, the majority of which were solids at ordinary temperatures.

(3) Mixed xylenes, under other conditions of temperature and contact surfaces, were converted into crude toluene, in



quantities approximating 64.0 percent of the possible theoretical.

(4) Mixed xylenes, under the influence of heat and iron surfaces, were decomposed quantitatively into amorphous carbon and gaseous products. Small particles of iron oxides and reduced iron were found in the deposited carbon.

(5) Activation of heated iron and carbon surfaces could be induced by treating with superheated steam during a short period, and afterwards slightly reducing with hydrogen.

(6) A deadening effect, opposite in characteristics to the above, was caused, when carbon dioxide, carbon monoxide, air or superheated steam was passed through the activated furnace. This condition seemed to be the same as is ordinarily described, as poisoning of the catalyser.

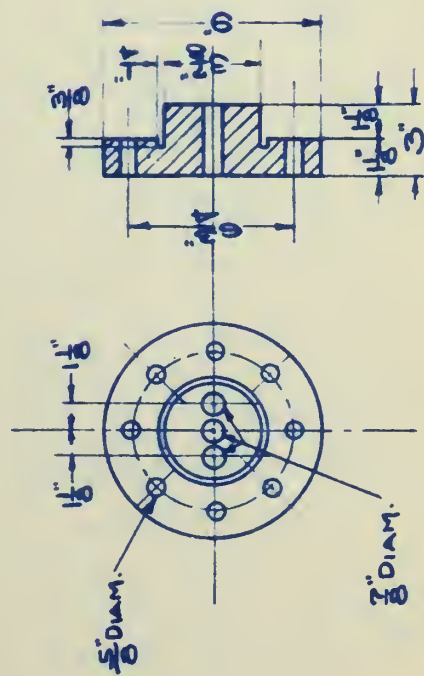
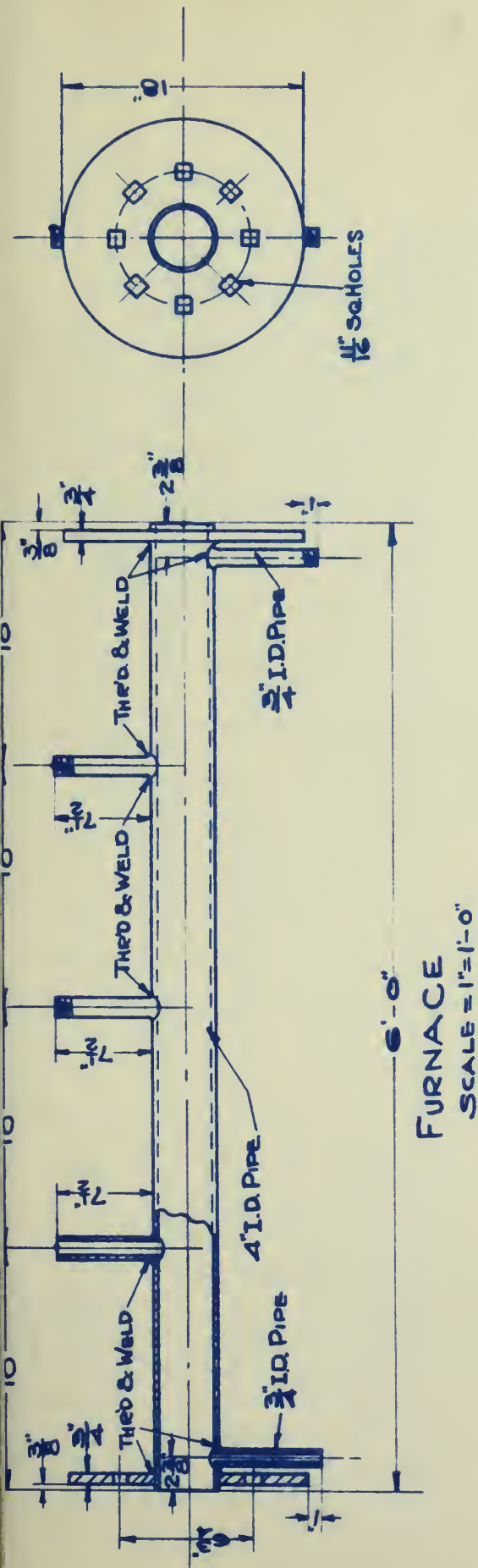
(7) The decomposition of ethylene was controlled so that practically pure methane, or mixtures of methane and ethane were obtained as end products.

(8) The following gaseous products were synthesised from mixed xylene: Ethylene, methane, ethane, acetylene and carbon oxides.

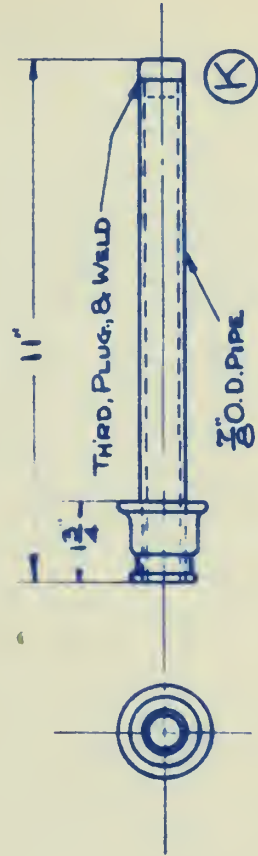
(9) Among the liquid products synthesised from mixed xylene:- n-hexane, cyclohexane, benzene, toluene, ditolyls, methylnaphthalene, and diphenylethane have been identified.

(10) The solids synthesised from mixed xylenes contained diphenyl, naphthalene, stilbene, methyl anthracene, p-diphenyl benzene, anthracene and methy derivatives.





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## II.

## EXPERIMENTAL WORK.

## 1. APPARATUS.

The essential parts of the apparatus are shown in the accompanying photographs and drawing. The complete outfit, being of a conventional type, requires little explanation with the possible exception of the furnace. It was made by taking six feet of four inch, No. 18 Byer's pipe, threading on flanges and thermo couple pockets and then having these joints acetylene welded to insure having no leaks under conditions of high temperature and pressure. The caps were cast particularly for this furnace and extended  $1\frac{1}{2}$  inches into the end of the pipe and were fitted with three, three-quarter-inch threaded openings leading into the furnace. The pipe was thinly coated with alundum cement; wound in five sections, each having 36.5 feet No. 14A chromel resistance wire and again coated with cement. It was surrounded by a wooden box twenty inches square and as long as the furnace, which contained the pulverized asbestos and Sil-O-Cel insulation. Each heating element, when connected directly across the 110 volt line, allowed a maximum current of 20 amperes to pass through but this could be reduced to 5 amperes by means of an external resistance connected in series at the switch board. At no time was more than 10 amperes allowed to go through the heating elements. By this means the heat of the furnace could be kept constant at any desired



temperature between 250 and 900<sup>0</sup> C. The top end was fitted with feed pipes for xylene, superheated steam and other gases, also with a pressure and reduced pressure gauge. On the exit at the bottom end was a safety relief valve, or constant pressure valve, which could be adjusted to let the gases escape into the line, leading to the gas meter, at any desired pressure. This outfit has been operated under 180 pounds pressure per square inch. The temperature was measured by means of a thermocouple made from six feet of No. 8 Chromel and alumel wire. The cold junction was kept at zero by means of a thermos bottle well and ice water, the e.m.f. was read on a millivoltmeter which had been standardized at known temperatures. By this method the temperature could be read accurately within four or five degrees. The thermocouple pockets (k) extended into the middle of the furnace and thus gave the temperature of the area where the largest volume of vapors passed.





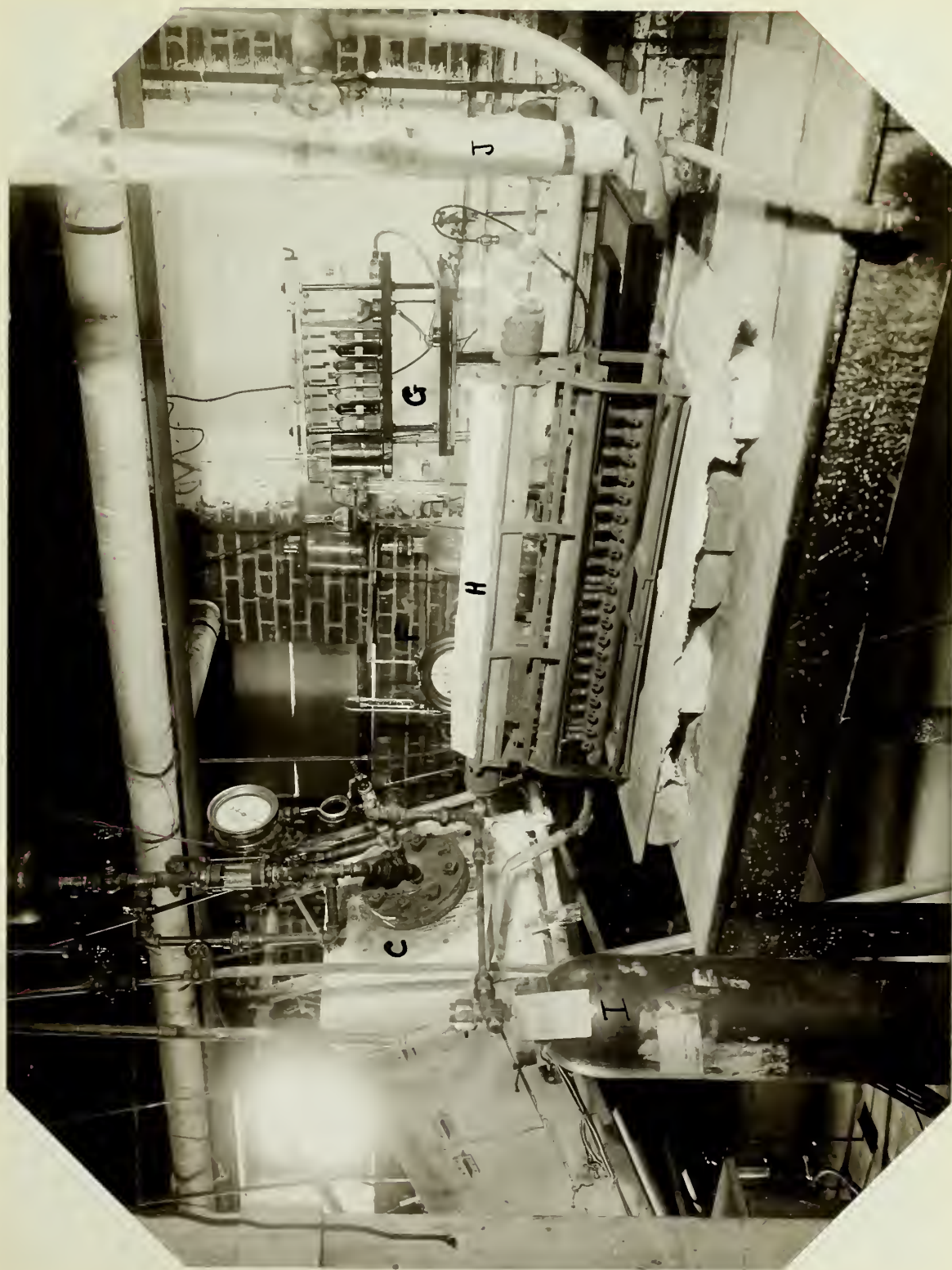


Fig. 1. Upper end of Furnace.





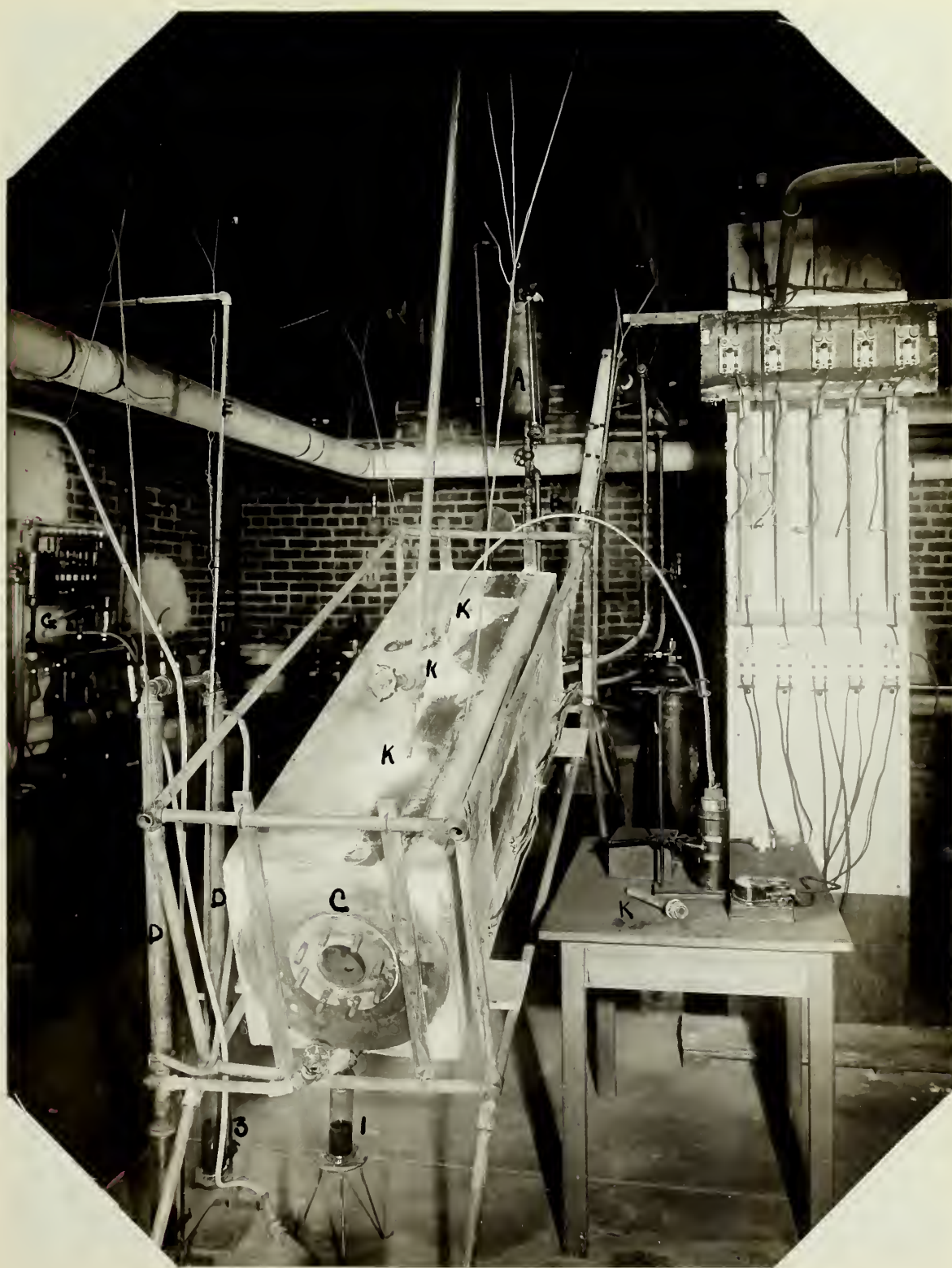


Fig. 2. Lower end of furnace.



## 2. METHOD OF OPERATION.

The mechanical arrangement of the apparatus is apparent from the explanation of the progressive steps of a typical run. The xylene was placed in the reservoir (A) fed by means of a regulating valve through the sight-glass, or bypass (B) into the upper end of the furnace (C). Here also, could be introduced gas, such as hydrogen, nitrogen, carbon dioxide or ethylene from the cylinder (I), or from the high pressure steam line (J) through the gas-fired superheater (H) could be introduced steam. Another attachment, not shown in the picture, permitted the use of compressed air. In passing down through (C) the vapors came into contact with the various contact surfaces used. The highest boiling condensate was collected in receiver (1) the medium oils in No. (2) while the gases, after passing through the water cooled condensers (D) were scrubbed with heavy oil in receiver (3). The gas leaving receiver (3) passed through pipe (E) to be measured by the meter (F) and was then burned, or analysed by means of the modified Orsat apparatus (G). When running under increased pressure, extra lengths of piping, fitted with a gate valve, were attached to the ends of the condensers. By keeping the lower valve closed and the upper one open, the condensate collected between them and could be easily removed, by closing the upper valve and opening the lower one, without causing any change in the pressure within the furnace.





### 3. METHOD OF ANALYSING PRODUCTS.

The condensable products were weighed, fractionated through a six-inch wash column of glass-beads, until all the liquid boiling below  $145^{\circ}\text{C}$  was removed. The liquid boiling above  $145^{\circ}\text{C}$ , designated in the following experimental results as high boiling product, was then transferred to an ordinary pyrex distilling flask and the fractionation continued until all but coke was driven over. These operations were performed by means of electrically heated furnaces similar to those fully described by Charlton.<sup>17</sup>

The solids obtained from the high boiling oils were purified and analysed by a combination of various methods, as described by Charlton,<sup>17</sup> Clark<sup>21</sup>, Cook<sup>22</sup> and others. These will be fully explained in a succeeding thesis now being prepared in these laboratories by Mr. Malecki.

The non-condensable or gaseous products were analysed by means of a modified Orsat apparatus which has been constructed in these laboratories. A full description of this apparatus will be submitted for publication to one of the technical journals. The carbon dioxide was removed by 35% potassium hydroxide; oxygen by potassium pyrogallate; acetylene by ammonical silver chloride; ethylene by bromine water; aromatics by 20% fuming sulfuric acid; hydrogen and carbon monoxide by combustion at  $280\text{--}300^{\circ}\text{C}$  with copper and ceric oxides; ethane and methane by slow combustion in pure oxygen; while the nitrogen was estimated by difference. It is realized





that an exact separation of acetylene and ethylene cannot be obtained in the above manner but by leaving the gaseous mixture in contact with the ammonical silver chloride solution during a constant time interval in each analysis, a relative idea of these two constituents can be obtained. A Complete analysis could be made in less than thirty minutes, except in cases where the carbon-monoxide content was high. Carbon monoxide seemed to poison the copper and ceric oxides and thus greatly retard this combustion.

#### 4. SPECIFICATION OF THE HYDROCARBONS USED IN THE INVESTIGATION.

The mixed xylene, the commercial product put on the market by the Barrett Co. in 10 gallon tin cans, was used in the major portion of this work. It was water-white, contained no suspended material, was free from moisture, had no foreign odor, practically all distilled between 137 and 142°C, and had a specific gravity of 0.8664, at 15.5°C.

The benzene, toluene and naphthalene used were the commercial products in stock at the chemistry store-room. They were not analysed or purified in any way. In fact, only a few runs were made with them, to try to check up on the results obtained from xylene, under similar conditions in the furnace.

#### 5. RESULTS OF PRELIMINARY RUNS.

By the term "run" is meant the operation of feeding



a definite quantity of material into the furnace, at any desired temperature, during a constant time interval. Or stated in another way, feeding the material at a constant rate; this rate was changed to suit the other conditions but was constant during any series of runs. After all the material had been passed into the furnace about thirty minutes were required for the final traces of the condensate to drain out and the evolution of gas to be completed.

In order to try out the effect of temperature and the iron furnace surface on the xylene a series of runs were made at atmospheric pressure, with 1000 grams of xylene, at each  $50^{\circ}\text{C}$  rise in temperature, between  $200$  and  $600^{\circ}\text{C}$ . Each run required one hour. In this series of nine runs, the loss was less than one percent, the gas given off was too small to warrant analysing, while the condensate proved to be almost entirely unchanged xylene. Naturally it was concluded, that the effect of the iron surface at various temperatures, was practically negligible and could, very conveniently, be neglected for all practical purposes in this investigation. However, before the work had proceeded very far, this was found to be an erroneous conclusion. The iron surface could be "activated" or "deadened" in such a way as to produce diversified results.



## 6. SERIES OF RUNS USING CHARCOAL SURFACES.

This series of runs were to ascertain the effects of iron and charcoal surfaces under similar conditions as recorded previously. A piece of sheet iron,  $3/16$  inches thick and five feet long, which had been drilled with  $5/8$ " holes  $3/8$ " apart, was made into a tube, which fitted snugly into the furnace. In this perforated tube was placed approximately two kilos of wood charcoal, which had been cut into cubes between  $1/2$  and  $3/4$  inch square.

In these runs 1000 gas. of xylene was used as before. The first run was made at  $250^{\circ}\text{C}$  and in it the loss of xylene amounted to 4 percent. This was no doubt due to absorption by the charcoal. As the temperature was raised, more moisture was driven from the charcoal and the percentage of carbon monoxide in the gas increased. Below  $450^{\circ}\text{C}$  very little change was noted in the recovered xylene, or in the volume of gas given off. In fact, the total loss of xylene was only about one to two percent. The results of the runs above  $450^{\circ}\text{C}$  are shown in Table No. I. In this table, as in all the following, the analysis of the escaping gas is given first; then the total amount of gas given off in the reaction, expressed in cubic feet; then comes the loss, in weight percent of the original xylene used in the run and finally a partial distillation analysis of the recovered condensate on the same basis. These cuts





are made at arbitrary temperatures best suited to the distilling flask and wash-column used. In closer analytical work, it was found that the maximum portion of the fraction passing over up to  $105^{\circ}\text{C}$  consisted of benzene, between  $105$  and  $130^{\circ}\text{C}$  to be toluene and between  $130$  and  $145^{\circ}\text{C}$  to be xylenes.

Of the product boiling above  $145^{\circ}\text{C}$ , 375 grams was distilled from an ordinary pyrex distilling flask and percentage boiling between different temperatures is shown in the summary.



TABLE I

Summary of runs through furnace, containing  $2\frac{1}{2}$  kilos of charcoal cubes. In each run 1000 gms. of xylene was used and required two hours to feed into the furnace.

No. of Run	20	21	22	23	24	25	26	27
Pressure lbs.	All Atmospheric							
Temperature C	450	500	550	600	650	700	750	800
Carbon Dioxide	6.9	10.2	6.4	1.6	0.2	0.2	0.0	0.1
Oxygen	7.2	2.8	1.7	1.3	0.5	0.4	0.4	0.1
Acetylene	0.0	0.4	0.2	1.2	1.0	0.4	0.3	0.2
Ethylene	0.1	0.2	0.3	3.4	4.3	2.2	1.7	1.4
Aromatics	0.0	0.1	3.1	12.2	8.0	3.1	2.7	1.6
Hydrogen	2.6	10.8	19.2	37.0	61.1	50.6	45.0	45.6
Carbon Monoxide	2.2	7.4	0.6	1.7	1.8	0.2	0.7	0.9
Ethane	2.2	1.0	4.8	7.1	3.2	2.3	0.8	0.0
Methane	0.7	0.9	12.6	23.9	19.2	25.7	39.4	48.3
Nitrogen	30.4	66.2	50.9	10.8	0.7	14.8	9.0	1.8
Total gas cu.ft.	0.2	0.2	0.2	1.0	2.3	6.9	8.4	8.0
Percentage Loss	6.0	2.0	5.0	7.0	22.5	23.5	34.0	50.0
Up to 105°C	...	...	...	...	#tr	#tr	13.0	5.0
105 to 130°C	...	...	...	...	...	15.5	16.0	8.7
130 to 145°C	94.0	98.0	95.0	93.0	73.5	54.0	19.4	24.1
Above 145°C	...	...	...	#tr	4.0	7.0	16.2	12.2
145 to 175°C	11.2							
175 to 225°C	8.8							
225 to 300°C	24.6							
300 to Coke	41.4							
Coke	13.9							



In the heavy oils boiling between 225 and 300°C a white solid separated out on standing; while between 300 and 400°C a yellowish solid was deposited; while above 400°C the product was a yellowish solid at ordinary temperatures. The fraction coming over around 450°C was a reddish tarry substance and the last traces driven off were dense red fumes.

In all the above runs more or less water was found in the condensate. This may have been held mechanically by the charcoal, or the result of reduction of some oxides, probably iron oxides.

The table shows very plainly the stability of xylene under these conditions, decomposition, in appreciable amounts commencing around 650°C while at 750°C the yields of the desired products is maximum. It is also interesting to note the change in percentage of ethane and methane with temperature. Methane being much more stable at higher temperatures. As would be expected, the total loss and amount of gas produced increases with rise in temperature. The nitrogen content of the first analyses is high, owing to the fact that the gas coming off was not sufficient to sweep the entire outfit free from air. All gas samples

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#Note. In all gas analysis nitrogen is estimated by subtracting the sum of all the constituents from 100. The abbreviation Tr. indicates a very small amount less than one percent. All distillation cuts are given in weight percent of the original xylene used.





were taken when the run was about three quarters completed. It was supposed that the conditions within the furnace, at that time would be as near representative as possible for the run. The gas was always analysed directly before passing through the meter. That is, the constituent ratio was not changed by allowing the gas to be stored, during varying periods, over liquid, before analysing.

When the series of runs were completed, the furnace was allowed to become cold and the cap removed from the exit end. The charcoal in the lower half of the furnace was entirely consumed, leaving a gray, fluffy ash; the top half did not seem to have been changed, except being somewhat more lustrous in appearance. Between the perforated tube and the walls of the furnace was a compact deposit of carbon, which made it somewhat difficult to remove the inner tube. As the furnace had been kept at a constant temperature for a considerable time before each run, it was concluded that this deposit was not due entirely to higher temperature right at the walls of furnace but that the iron surface was in some way or other promoting decomposition of the xylene.

The next series of runs were made over  $2\frac{1}{2}$  kilos of charcoal cubes. These were cut in sizes varying from  $\frac{3}{4}$  inches to  $\frac{1}{4}$  inch square. The larger size, being placed in the furnace near the inlet and the smallest at the exit end. By this means more surface was exposed to the outgoing vapors. The furnace was



then closed and live steam at 125 pounds pressure was turned on to make sure that there were no leaks in the outfit. It was found out later that steaming the charcoal greatly modified its activity in decomposition processes.



TABLE II.

Summary of runs over  $2\frac{1}{2}$  kilos of charcoal cubes, which had been subject to live steam at 125 pounds pressure, before the furnace had been heated up. 1000 gms. of xylene used per run requiring two hours.

No. of Runs	30	31	32	33	34	35	36
Pressure lbs.	Atm	Atm	Atm	Atm	Atm	Atm	Atm
Temperature C.	550	600	700	665	625	600	550
Carbon Dioxide	0.9	1.4	0.9	0.0	0.1	0.0	0.0
Oxygen	4.4	6.0	0.2	0.3	0.1	0.0	0.4
Acetylene	1.6	0.8	0.8	0.7	0.9	0.5	0.3
Ethylene	1.8	3.0	0.2	0.1	0.0	0.0	0.2
Aromatics	0.7	12.6	1.0	1.4	1.0	1.0	1.0
Hydrogen	28.4	29.0	75.2	71.9	75.8	72.9	79.6
Carbon Monoxide	0.3	0.8	5.7	3.0	0.4	0.2	0.1
Ethane	20.5	0.0	6.7	1.2	1.8	0.0	0.0
Methane	12.6	32.0	6.6	21.5	18.4	24.1	17.5
Nitrogen	28.8	14.4	2.7	0.0	1.5	1.3	0.9
Total gas cu.ft.	0.3	0.7	4.0	25.6	25.4	25.2	18.0
Percentage less	+	4.0	38.7	100.0	100.0	100.0	84.5
Up to 105°C	tr	tr	6.5	...	...	...	10.0
105 to 130°C	25.3	15.0	1.0	...	...	...	3.0
130-145°C	72.5	77.7	49.8	...	...	...	0.0
Above 145°C	1.8	3.3	4.0	...	...	...	2.7

In run 30 it is interesting to note the amount of ethane formed. Also, these conditions seemed most favorable for the





production of the toluene fraction. As the temperature rose, the toluene fraction became less, while the hydrogen content of gas greatly increased. Near the end of run 32, the temperature fell rapidly to  $655^{\circ}\text{C}$  due to a different reaction taking place in the furnace. At the same time a marked increase was noted in the gas produced while the condensate decreased. Runs 33, 34, 35 and 36 were made on decreasing temperature conditions. As the table indicates, the destruction of xylene was complete, hydrogen, methane and carbon being the final products. As the temperature was lowered, to ascertain at how low a temperature this reaction would continue, some traces of condensate was obtained at  $550^{\circ}\text{C}$ . As the temperature decreased from this point the condensate increased.

The current was shut off and the furnace openings closed, so that no air could enter the outfit. After standing for four days the furnace was again heated up, without any change having been made in any particular from the previous conditions, and a series of runs made as the temperature increased. This was to see if the xylene would be again completely decomposed to gas and carbon, and to ascertain, if possible, at what temperature this reaction took place. The runs made at 250, 270, 325, 365, 400, 430, 450 and  $470^{\circ}\text{C}$  indicated very little reaction and practically no change, or loss in the xylene. When the temperature of complete decomposition was reached hydrogen from a cylinder was introduced at various rates to see if it was possible to stabilize any of the products by means of excess hydrogen from another source. The results show that this was in a small measure possible.



TABLE 3.

Summary of runs over charcoal and deposited carbon, which had previously given no condensate. 1000 grams of xylene used per run, requiring one hour. Hydrogen introduced from cylinder at arbitrary rate.

No. of Run	45	46	47	48	49	50
Gas introduced	...	...	H <sub>2</sub>	H <sub>2</sub>	H <sub>2</sub>	Air
Pressure (lbs)	Atm.	Atm	21	25	15	5
Temperature °C.	500	550	650	600	500	500
Carbondioxide	0.0	0.0	0.0	0.0	0.0	3.5
Oxygen	1.0	0.0	0.0	0.0	0.0	0.3
Acetylene	0.0	0.7	6.7	0.0	0.5	0.0
Ethylene	0.7	0.3	0.1	0.6	0.1	0.1
Aromatics	1.2	1.4	1.0	1.0	1.0	0.6
Hydrogen	82.0	80.0	65.6	67.6	74.8	69.9
Carbon Monoxide	0.7	0.1	0.3	0.0	0.0	5.1
Ethane	0.4	1.9	0.0	0.0	0.0	4.1
Methane	13.6	13.3	26.7	28.7	21.9	7.0
Nitrogen	0.4	2.3	0.0	2.1	0.0	9.4
Total gas cu.ft.	3.0	28.0	25.5	20.3	10.0	1.0
Percentage Loss	20.0	100.0	77.6	77.0	30.0	66.0
Up to 105°C.	1.0	...	2.0	tr.	tr.	...
105 to 130°C.	...	...	20.4	23.0	53.0	...
130 to 145°C.	75.5	...	...	...	17.0	44.0
Above 145°C.	3.5	...	...	...	...	...



Runs 45 and 46 corresponded to the results of the previous series. Runs 47, 48 and 49 were made under the same conditions with the exception that hydrogen was added from a cylinder, in a rapid stream, calculated to keep the atmosphere in the furnace, principally hydrogen. This gave conditions best suited to the formation of the toluene fraction. It would have been interesting to carry this investigation further under these conditions but so much xylene had been decomposed that the furnace was plugging up with deposited carbon. At this point 8 cubic feet of air was passed through the furnace, while heated to  $500^{\circ}\text{C}$ , to see if some of the carbon could be oxidized and thus removed. Several analyses were made on the issuing gases and as high as 12.0% carbon dioxide was found. It was soon demonstrated that this method of carbon disposal was too slow, so the air was discontinued. Run No. 50 at  $500^{\circ}\text{C}$  was with pure xylene, but the furnace was so filled up with carbon that it required a pressure of five pounds, built up from the decomposition of xylene, to force any gas through. It can be plainly seen that some marked change had taken place in the furnace. No toluene was obtained and all the condensate collected proved to be unchanged xylene. In other words, the oxygen and possibly the nitrogen also, had poisoned or slowed down the activity of the furnace. It was found by other methods that charcoal, after being heated to the neighborhood of  $700^{\circ}\text{C}$  allowed to cool, out of contact with air, would take up air very rapidly. By again heating, the oxygen came off slowly in the form of carbon oxides, the dioxide





being given off at lower temperatures and as the temperature increased, carbon monoxide was the chief product. It is doubtful, if all the oxygen taken up could be driven off at temperatures of  $700^{\circ}\text{C}$  even in the presence of hydrogen. Diminishing amounts of moisture, being driven off, even after the treatment had continued several days.

At the end of these runs, the furnace was so firmly plugged with deposited carbon, that it was impossible to remove the perforated tube containing the charcoal. In fact, this had to be broken into pieces to be taken out of the furnace.

The next series of runs was made with a view of increasing the toluene fraction. As before, charcoal cubes were prepared and placed in the furnace by means of a tube made from ordinary brown wrapping paper. The gradation in size in the charcoal cubes was the same as previously and the same quantity used. While heating the furnace, hydrogen was introduced, to try to reduce all oxides at temperatures as low as possible. As previously, moisture and a rancid smelling liquid was driven off the charcoal as the temperature increased. In this series of runs the rate of feed was decreased to 500 gms. of xylene per hour. At lower temperatures no appreciable change took place, and only in the neighborhood of  $500^{\circ}\text{C}$  were any results obtained worth tabulating.



Table 4.

Summary of runs over 2 kilos charcoal placed in furnace by means of paper tube, 1000 gms. xylene used per run, fed at the rate of 500 gms. per hour. Furnace had been heated under reducing conditions. Results of high boiling fraction was obtained from 225 gms. product of the series.

No. of Runs	53	54	55	56	57	58	59	60
Gas Introduced	H <sub>2</sub>	H <sub>2</sub>	...	...	...	H 2	...	Steam
Pressure Lbs.	Atm	Atm	Atm	Atm	Atm	Atm	Atm	Atm
Temperature °C.	600	650	625	650	700	750	750	750
Carbon Dioxide	1.3	0.5	1.0	0.0	0.0	0.0	0.0	20.2
Oxygen	0.3	0.1	0.6	0.5	0.1	0.1	0.0	0.0
Acetylene	0.3	0.1	0.8	0.3	0.1	0.3	0.2	0.0
Ethylene	0.1	1.5	1.1	0.8	1.4	1.5	1.3	0.0
Aromatics	0.6	0.8	3.4	4.1	2.2	1.5	2.2	3.8
Hydrogen	83.8	79.0	50.6	48.4	42.2	44.4	34.4	59.0
Carbon Monoxide	1.0	2.3	3.9	1.6	0.7	0.4	0.8	1.2
Ethane	0.0	0.0	5.5	0.0	0.0	0.0	0.0	0.9
Methane	9.1	16.6	22.1	41.5	48.9	48.0	58.8	12.8
Nitrogen	3.5	0.0	11.0	3.0	6.4	3.8	2.3	2.1
Total Gas Cu.ft.	5.2	8.0	1.5	3.0	6.8	10.2	10.0	13.4
Percentage Loss	6.0	20.0	12.0	8.0	23.0	25.0	33.0	20.0
Up to 105°C	...		1.0	1.0	7.0	7.0	8.0	tr
105 to 130°C	...		18.0	40.0	45.0	56.0	43.0	10.6
130 to 145°C	91.0		66.0	43.0	26.0	5.0	2.0	64.4
Above 145°C	3.0		3.0	8.0	9.0	7.0	14.0	5.0
145 to 170°C	12.8							
170 to 225°C	13.3							
225 to 325°C	44.4							
325 to Coke	20.4							
Coke	8.8							



The results, although differing in many details, show fair agreement with the previous runs. The one striking difference is that the percentage of hydrogen in the issuing gas is approximately one-half as much as previously. In run 59 the hydrogen was admitted slowly from the tank and seems to have materially increased the toluene fraction. This is in direct contradiction to the results obtained by Cobb and Hollings. They found that the presence of hydrogen when passing toluene through red-hot coke, greatly increased the decomposition of toluene to benzene. Of course, there are many other conditions, in the two sets of experiments which are vastly different, and which play an important part. Although, it may be possible that the largest percent of this increase is due to benzene, which was stabilized by the hydrogen. In run 60, the steam superheated to  $900^{\circ}\text{C}$  was admitted slowly during the run. The total water condensed amounted to 1020 gms. The stabilizing effect of steam is very noticeable, it seems to have lessened all the various conditions which had been promoting decomposition.

#### 7. SERIES OF RUNS THROUGH IRON FURNACE.

At this stage of the investigation, it was decided to examine further the effects of the iron surface of the furnace, on xylene. Up to this point so many contradictory results had been obtained, and so many factors had influenced the reactions, it was necessary to prove definitely what part the iron surfaces





took in the reactions. Accordingly, the furnace was allowed to cool, the cap removed and the charcoal withdrawn. The furnace walls were thoroughly cleaned with a wire brush, the cap replaced and the furnace heated up while superheated steam was passing through it. The steam was continued for some hours and until the furnace had reached a temperature of  $650^{\circ}\text{C}$ .



TABLE 5.

Summary of runs through the furnace without any charcoal. The furnace had been heated to  $640^{\circ}\text{C}$  while superheated steam was passing through. 500 gms. xylene was used in each run, which required one hour.

No. of Run	61	62	63	64	69	70	72	74
Gas introduced	Steam	...	$\text{H}_2$	...	...	$\text{H}_2$	$\text{H}_2$	$\text{CO}_2$
Pressure lbs.	Atm.	Atm.	Atm.	Atm.	Atm.	35	140	Atm.
Temperature $^{\circ}\text{C}$ .	650	675	650	625	660	650	625	600
Carbon Dioxide	25.1	1.2	0.3	0.4	0.3	0.2	0.3	53.8
Oxygen	0.7	1.3	0.2	1.0	0.4	0.2	0.1	0.3
Acetylene	0.0	0.3	0.2	0.4	0.7	0.5	0.2	0.1
Ethylene	1.2	1.7	0.2	0.3	0.8	0.2	0.5	0.3
Aromatics	2.5	10.0	0.6	0.1	0.2	1.0	0.7	0.3
Hydrogen	56.3	26.8	74.7	82.8	82.4	62.9	55.0	20.2
Carbon Monoxide	3.0	1.2	13.9	2.5	5.7	2.9	1.0	19.8
Ethane	1.0	3.8	2.0	0.2	0.0	0.0	0.0	0.0
Methane	6.6	50.0	6.3	12.7	9.5	32.0	40.8	5.2
Nitrogen	3.6	3.7	1.6	0.0	0.0	0.0	1.3	0.0
Total Gas cu.ft.	5.1	1.5	13.6	16.4	17.0	12.0	6.5	26.5
Percentage Loss	12.0	10.0	60.0	100.0	100.0	99.5	99.5	55.0
Up to $105^{\circ}\text{C}$	...	2.0	tr			...	...	...
105 to $130^{\circ}\text{C}$	tr	22.0	12.0			...	...	...
130 to $145^{\circ}\text{C}$	86.0	61.0	25.0			tr	tr	44.0
Above $145^{\circ}\text{C}$	2.0	5.0	3.0			...	....	1.0



In this series of experiments many interesting details are clearly demonstrated. In run 61 the protecting action of steam is clearly shown, also the percentage of carbon dioxide is slightly greater than in the case where the furnace contained charcoal. In this case the carbon must be coming from the decomposed xylene. In No. 62 the steam was discontinued and the run made at once without any change being made in the furnace with the exception of a slight rise in temperature. Here the decomposition of the xylene was greater but the loss was even less, more going to lighter boiling products. Run 63 was made directly after 62 without any change except a lowering of the temperature  $25^{\circ}\text{C}$ . With this run, hydrogen from a cylinder was introduced in a slow stream intended to maintain reducing conditions in the furnace, with hydrogen, other than that from the decomposition of xylene. In former runs, it was found that after the furnace and charcoal had been steamed, and then reduced to a certain degree by hydrogen, that the furnace reached a condition, which for the sake of distinction, we might call "activated". In this condition the tendency was for complete destruction of the liquid hydrocarbons into hydrogen, carbon and some methane. Run 63 was made in order to see if this activated condition could be obtained without the presence of charcoal. When the run was about three-quarters completed, a great increase in the outcoming gas was noticed and the condensate gradually diminished and finally stopped. When this happened, the furnace temperature fell considerably. After waiting during thirty minutes, run 64 was made to see if this "activated"





condition still continued, the results are conclusive.

The furnace was now allowed to become cold, out of contact with air, and after standing a few days was opened. On removing the deposited carbon, which was intensely black and fluffy, it was found to weigh 870 gms. or practically the theoretical amount possible from the 960 gms. of xylene decomposed. On further analysis, however, the carbon was found to contain approximately 11% iron, which was found to be a mixture of the magnetic oxide, and other oxides along with some fine particles of reduced iron. The magnetic oxide, seemed to form the largest percentage.

After thoroughly cleaning out all carbon by means of a wire brush, the furnace was heated up to  $640^{\circ}\text{C}$  and a series of runs made to see if it was still activated. Run 65 at  $635^{\circ}\text{C}$  was made with xylene alone. The results corresponded very closely with run 62, while runs 66 and 67 at 650 and  $675^{\circ}\text{C}$  were made with hydrogen. The results were similar to run 63. At this stage it was decided to pass super-heated steam through the furnace until fully oxidized or deadened, then reduce somewhat with hydrogen from a cylinder and then start another run. Run 68 was made at  $665^{\circ}\text{C}$  and had only been going a few minutes when a sudden increase in the gas given off was noticed and the condensate ceased. Run 69 was made to confirm these results.

It was now desirable to see if any of the products of decomposition of the xylene could be stabilized, by means of increasing the hydrogen concentration. Accordingly, in run 70, the furnace was placed under a pressure of 35 pounds per



square inch, with hydrogen, before the xylene was admitted. In run 72, the pressure with hydrogen was increased to 140 pounds, before starting, but after the xylene was admitted, the decomposition gases were sufficient to keep the pressure at the desired point. These two runs show that it was not possible to stabilize even benzene under these conditions. In the next run at 600°C carbon dioxide was passed through slowly and so changed the conditions in the furnace that much of the xylene came through unchanged. The effects of carbon dioxide are somewhat analogous to those of steam under similar conditions. It is possible the carbon dioxide, or more probably the carbon monoxide, formed in both cases, is responsible for this inhibition. This series demonstrates, that the catalyst, whatever it may be, appears to possess the capacity for invigoration. It did not prove what this catalyst was, because even minute decomposition of xylene would deposit carbon, and this carbon may have promoted the decomposition reaction, or again, it may have acted only as a promoter to the iron surfaces.

#### 8. SERIES OF RUNS THROUGH COPPER LINED FURNACE.

It was considered more easy to get rid of the influence of iron than of carbon. Accordingly a tube was made from No. 18 sheet copper, which fitted snugly inside the iron furnace and extended under the ends of the caps. In this manner all iron surfaces including the thermo couple pockets, were covered with copper. The influence of copper on the decomposition of xylene is shown in table 6. The copper was oxidized with steam and reduced with hydrogen from the cylinder as in previous runs.



TABLE 6.

Summary of runs through copper lined furnace 500 gms. of xylene being used per run per hour.

No. of run	75	76	77	78	79
Gas introduced	...	...	Steam	..	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	Atm
Temperature °C	575	625	610	610	610
Carbon Dioxide	2.8	0.7	17.4	3.8	not
Oxygen	0.6	0.3	2.0	2.4	run
Acetylene	0.3	0.4	0.4	0.4	
Ethylene	0.9	1.2	1.6	1.4	
Aromatics	0.8	2.4	2.4	5.4	
Hydrogen	69.1	76.0	62.8	40.4	
Carbon Monoxide	14.5	5.2	4.1	2.6	
Ethane	2.7	2.3	0.9	0.0	
Methane	4.2	11.1	8.0	31.9	
Nitrogen	4.1	0.4	0.4	11.7	
Total gas cu.ft.	3.8	4.7	3.0	0.7	8.5
Percentage Loss	37.5	32.5	12.0	7.5	12.5
Up to 105°C	0.0	0.0	0.0	0.0	0.0
105 to 130°C	3.0	5.0	10.0	25.0	7.5
130 to 145°C	55.5	62.5	75.0	63.5	76.5
Above 145°C	4.0	tr	3.0	4.0	3.5





These results show that somewhat greater decomposition took place in the copper than in the iron furnace. By comparing runs 61 and 76, it can be seen that steam exerted similar influences in each case. Run 79 was made after reducing the furnace some time with hydrogen. It was not found possible to activate the copper lining so that complete decomposition took place as happened in the case of iron. After cooling the furnace was opened and only a gram or so of carbon was found scattered along the bottom. In this case it would appear that the carbon had disappeared in gaseous form rather than being deposited. The copper surface was highly reduced and in a clean condition.



TABLE 7.

Summary of runs through copper lined furnace containing  $2\frac{1}{2}$  kilos of charcoal cubes, each run consisted of 200 gms. of xylene, and was fed through furnace in one hour. The percentages given for the high boiling (above 145) were obtained from 50 gms. obtained in these runs.

No. of Run	81	82	83	84	85	86	88
Gas Introduced	...	...	...	...	Steam	...	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	Atm	Atm	Atm
Temperature °C.	600	630	680	750	735	750	765
Carbon Dioxide	2.9	1.8	1.0	0.8	20.7	2.0	0.6
Oxygen	0.5	0.4	0.5	0.5	0.6	1.1	0.4
Acetylene	0.6	0.2	0.5	0.1	0.3	0.6	1.0
Ethylene	2.3	3.5	1.4	1.4	1.4	1.2	2.4
Aromatics	0.5	2.5	0.4	0.7	1.0	1.2	1.6
Hydrogen	34.2	18.2	36.3	31.0	43.7	36.5	44.5
Carbon Monoxide	17.9	27.4	10.2	9.6	16.7	11.5	13.8
Ethane	10.8	7.5	0.0	0.0	4.2	2.0	0.8
Methane	20.0	30.4	45.3	57.2	9.3	39.5	35.0
Nitrogen	10.3	8.1	4.4	0.0	0.8	4.4	0.0
Total gas cu.ft.	1.3	1.2	3.3	3.2	15.5	4.5	4.0
Percentage Loss	25.0	17.0	50.0	70.0	55.0	78.0	63.5
Up to 105°C	2.5	2.0	10.0	10.0	5.0	18.0	18.0
105 to 130°C	25.0	18.0	20.0	15.0	8.0	0.5	12.5
130 to 145°C	45.0	55.0	15.0	0.0	26.0	0.0	0.0
Above 145°C	2.5	8.0	5.0	5.0	6.0	3.5	6.0
145 to 170°C	45.5						
170°C to 225°C	4.9						
225 to 300°C	16.5						
300 to 400°C	21.3						
400 to Coke	5.6						
Coke	6.2						



In this series of runs no exceptional incidents were noticed. Several runs were made between 86 and 88 with and without hydrogen, in an effort to get the furnace in an activated condition but without success. Run 88, with hydrogen, indicates that here the hydrogen cut down the actual loss by stabilizing the lower boiling fractions.

The next series of runs were made, over oxidized Illium turnings. These turnings had been heated to  $800^{\circ}\text{C}$  and oxidized by means of oxygen from a cylinder. Three and one-half kilos of oxidized turning were mechanically mixed with small pices of pumice stone and by means of a paper tube were placed inside the furnace. Table 8 summarizes the results.





TABLE 8.

47.

Summary of runs through copper lined furnace over  $3\frac{1}{2}$  kilos of oxidized Illium turnings suspended in pumice stone. 200 gms. xylene used per run per hour.

High boiling percentages given from 90 gms. obtained in runs.

No. of Run	91	92	93	94	95	96	97
Gas Introduced	...	...	...	...	...	H <sub>2</sub> .	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	Atm	30	Atm
Temperature °C	525	600	650	700	785	785	785
Carbond Dioxide	not	6.8	not	1.7	1.3	0.6	0.3
Oxygen	run	1.4	run	0.8	0.6	1.0	0.1
Acetylene		0.8		1.3	0.7	0.8	0.8
Ethylene		4.0		3.0	1.8	1.8	1.8
Aromatics		2.0		2.0	2.0	1.6	1.8
Hydrogen		45.8		33.7	36.2	40.9	50.2
Carbon Monoxide		5.6		14.8	4.2	4.2	11.2
Ethane		1.9		1.5	0.0	0.0	0.0
Methane		25.3		37.4	53.2	49.1	34.2
Nitrogen		6.4		3.8	0.0	0.0	0.0
Total Gas Cu. Ft.	0.2	0.5	1.3	2.4	3.5	4.5	8.0
Percentage Loss	tr	3.0	15.0	29.0	76.0	88.5	73.5
Up to 105°C	5.0	4.0	tr	6.0	7.0	8.0	3.0
105 to 130°C	8.0	10.0	12.0	40.0	7.0	0.0	10.0
130 to 145°C	84.0	79.0	77.0	17.0	0.0	0.0	6.5
Above 145°C	3.0	4.0	6.0	8.0	10.0	3.5	7.0
145 to 170°C	17.7						
170 to 225°C	11.1						
225 to 300°C	16.6						
300 to 400°C	22.2						
400 to Coke	22.2						
Coke	10.2						



The results with Illium oxide, show that in the region of  $700^{\circ}\text{C}$  the decomposition of xylene into the toluene fraction is maximum. Above this temperature the lower boiling fractions decrease with a slight increase in the higher boiling compounds. It is very probable that much more interesting results would have been obtained by using the Illium turnings without oxidixing. The pieces of pumice when broken up, showed that hydrocarbon vapors had penetrated them throughout. They contained very fine particles of carbon in the centre of even the largest pieces.

The next runs were made to find out the effects of finely divided nickel under similar conditions. Accordingly small pieces of pumice, about  $1/2$  inch square, were dipped in heated nickel nitrate. The nitrate was heated in a nickel crucible until most of the water of crystallization was driven off, and the fluid became syrupy. The cubes were then dried at  $120^{\circ}\text{C}$  for a few hours, placed in paper tube and inserted into the copper lined furnace. The temperature was ~~not~~ raised to  $500^{\circ}\text{C}$  and the nickel reduced with hydrogen from a cylinder. Five pounds of nickel nitrate was used. The results are given in table 9.



TABLE 9

Summary of runs using nickel, which had been reduced from the nitrate, on pumice cubes. 200 gms. xylene used per run per hour.

No. of Run	100	101	102	103	104	105	106	107
Gas Introduced	...	...	...	...	...	H <sub>2</sub>	Steam	...
Pressure lbs.	Atm	Atm	Atm	Atm	Atm	Atm	Atm	Atm
Temperature °C.	500	550	605	665	700	730	735	735
Carbon dioxide	0.8	0.7	0.5	0.7	0.7	0.1	7.0	not
Oxygen	0.0	0.3	0.5	0.7	0.7	0.4	0.4	run
Acetylene	0.0	1.0	0.6	0.9	0.6	1.1	0.7	
Ethylene	0.4	1.0	1.7	2.0	2.2	0.7	1.1	
Aromatics	0.2	1.2	1.0	1.6	1.2	1.2	1.1	
Hydrogen	57.3	70.5	63.8	63.3	53.8	82.0	62.3	
Carbon Monoxide	10.3	4.6	5.6	3.6	5.0	2.2	15.5	
Ethane	0.0	0.0	0.0	0.0	0.0	0.0	2.7	
Methane	23.9	21.2	24.4	28.6	33.6	9.3	5.0	
Nitrogen	8.1	0.0	1.9	0.0	2.2	3.0	4.2	
Total Gas Cu.Ft.	3.2	3.6	2.5	3.0	3.7	15.0	13.2	8.0
Percentage Loss	64.0	63.5	42.0	49.0	64.0	97.5	71.0	98.0
Up to 105°C	...	...	...	2.5	2.5	2.5	...	...
105 to 130°C	tr.	tr.	3.5	15.5	19.0		10.0	tr
130 to 145°C	33.0	33.5	50.5	29.0	9.5		17.5	tr
Above 145°C	3.0	3.0	4.0	4.0	5.0		1.5	...





It is quite apparent that nickel, under these conditions, did not promote the formation of high boiling compounds but seemingly promoted complete destruction of the condensable hydrocarbons. In each of these runs considerable moisture was collected. Only small traces of unoxidized nickel was to be found on the pumice.

The pumice resembled chunks of coke embeded in lamp black. The burning gas gave a distinct nickel flame.

At the conclusion of this series of experiments the copper lining was found to be in a poor state of repair. In the hotter part of the furnace it had crystallized and fallen to pieces leaving considerable surface of the iron furnace again exposed to the reactions. Near the ends some areas of it was found to be highly reduced while mixed with these were spots covered with a thick layer of oxide. It is quite certain that in the last of the previous series of runs, the iron surfaces were playing a part. The copper lining was ~~not~~ removed and replaced by one of tinned-copper, the tinned surface being on the inside. This tube was lap-welded and riveted and made to fit snugly into the furnace, covering all iron surfaces.

#### 9. SERIES OF RUNS USING TINNED-COPPER LINING IN FURNACE.

In the preliminary runs on this lining the temperature was not raised much above  $605^{\circ}\text{C}$ , in order to prevent scaling off the tinned surface. The results are given in Table 10.



TABLE 10.

Summary of runs using tinned-copper lining in furnace.

200 gms. of xylene used per run per hour.

No. of Run	110	111	112	113
Gas Introduced	...	...	...	...
Pressure lbs.	Atm	Atm	Atm	Atm
Temperature °C.	425	500	550	625
Carbon dioxide	Not	2.0	1.3	1.0
Oxygen		0.7	1.1	0.9
Acetylene	run	0.2	0.4	1.0
Ethylene		1.7	2.1	9.2
Aromatics		1.0	5.3	2.7
Hydrogen		71.4	53.0	29.4
Carbon Monoxide		6.5	5.0	3.6
Ethane		0.0	0.0	0.0
Methane		12.9	31.4	58.0
Nitrogen		3.5	0.4	1.2
Total gas cu.ft.	0.2	0.6	1.0	1.5
Percentage Loss	12.0	8.0	14.0	27.0
Up to 105°C	...	2.5	2.0	5.0
105 to 130°C	...	tr	12.0	25.0
130 to 145°C	84.5	86.5	69.5	36.0
Above 145°C	3.5	3.0	2.5	7.0



These results indicate that in the neighborhood of 700°C a tinned surface in the furnace would be favorable for the production of toluene and benzene from xylene.

The next series of runs were made to find out the effects on xylene, of finely divided nickel-oxide on charcoal under various conditions. The  $2\frac{1}{2}$  kilos of charcoal cubes, which had been used previously in the copper lined furnace, were heated at 700°C in an atmosphere of hydrogen, allowed to cool, - out of contact with air, - then dipped in a thin paste containing one pound of nickel oxide. After being dried at 110°C they were placed in a paper tube and inserted in the furnace, in the usual manner. In this series the nickel oxide was not reduced with hydrogen before the runs were started. The results are tabulated in Table 11.





TABLE 11.

Summary of runs over nickel oxide on charcoal. 200 gms.  
of xylene used per run per hour. Tinned copper lining in furnace.

No. of run	120	121	122	123	124	125	126.
Gas introduced	...	...	...	...	...	H <sub>2</sub>	Air
Pressure lbs.	Atm	Atm	Atm	Atm	Atm	15	Atm.
Temperature °C.	475	525	565	600	650	665	665
Carbon Dioxide	1.0	0.0	1.0	0.8	0.5	0.0	0.4
Oxygen	1.0	0.4	0.8	0.9	0.8	0.0	0.5
Acetylene	0.1	0.4	0.0	0.1	0.1	0.0	0.0
Ethylene	0.3	0.5	1.0	1.0	0.5	0.4	0.9
Aromatics	0.3	0.3	0.6	0.7	0.5	0.6	0.5
Hydrogen	64.0	65.4	67.6	66.8	80.0	81.5	77.3
Carbon Monoxide	8.5	5.9	6.4	8.0	5.8	3.4	5.3
Ethane	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Methane	24.8	23.6	18.8	19.4	11.8	14.1	15.1
Nitrogen	0.0	3.4	3.8	2.3	0.0	0.0	0.0
Total Gas cu.ft.	3.2	3.9	4.0	4.5	7.0	9.0	6.0
Percentage Loss	82.5	77.5	63.5	83.0	98.0	100.0	96.0
Up to 105°C	0.0	4.0	tr	tr	...	...	tr
105 to 130°C	tr	tr	6.0	9.0	...	...	tr
130 to 145°C	14.5	13.5	25.0	3.0	2.0	...	tr
Above 145°C	3.0	5.0	5.5	5.0	...	...	...



In each of the above runs three to five grams of water were collected. The combination of hickel oxide and charcoal gave results similar to the iron oxides and charcoal. Before run 125 the outfit had been reduced for one hour with hydrogen under 15 pounds pressure. Before run 126 nine cubic feet of air had been passed through the hot furnace but was discontinued during run. When the furnace was cleaned after this series, it was found that practically all the tin surface had scaled off the copper tube. Thus copper as well as tin could have exerted an influence on the last runs.

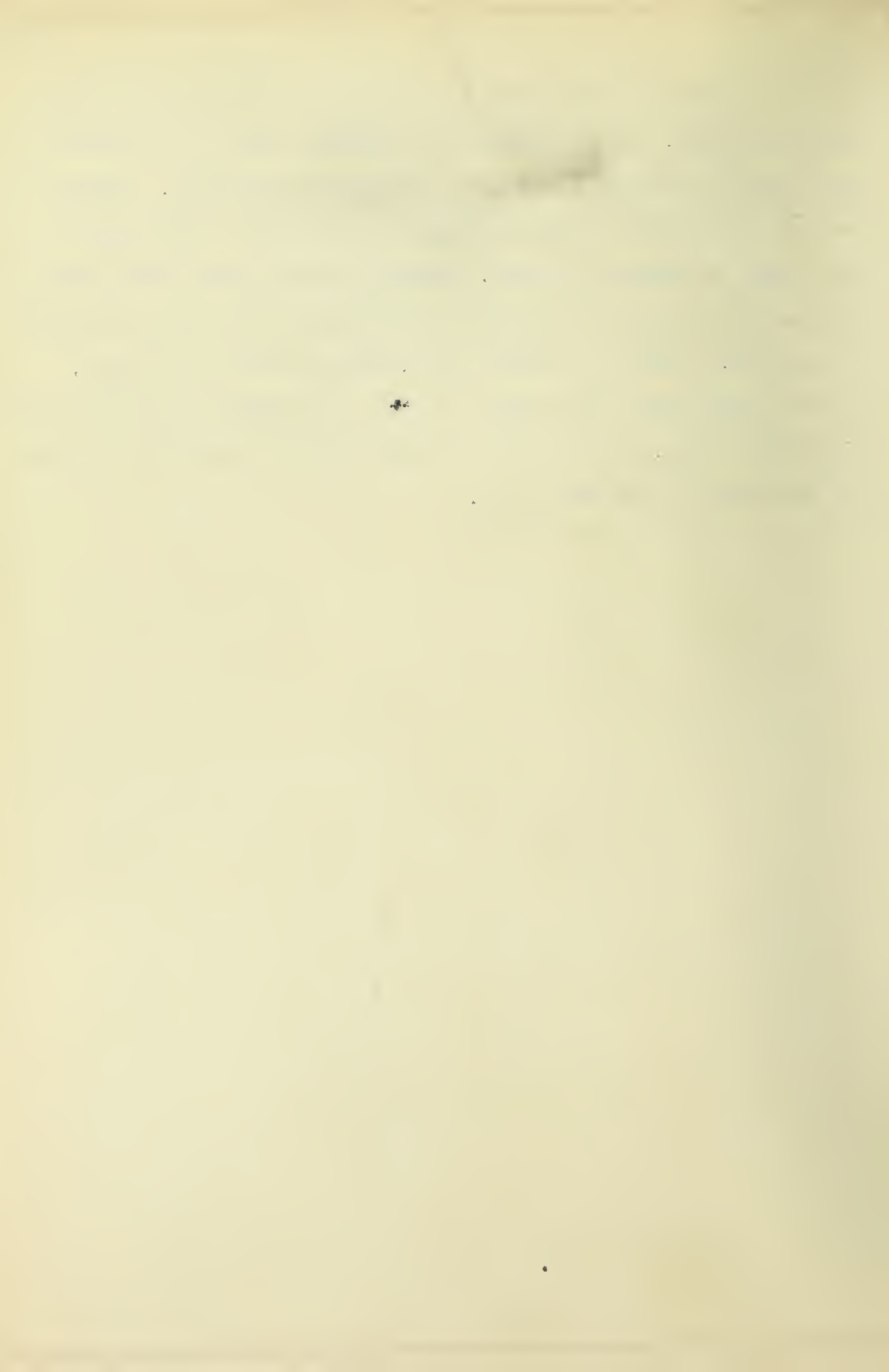


TABLE 12.

Summary of runs through copper lined furnace over 1/2 pound of molybdenum powder, mixed dry among small pieces of pumice stone. 200 gms. of xylene used per run per hour.

No. of run	130	131	132	133	134
Gas Introduced	...	...	...	...	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	60
Temperature °C.	550	600	650	680	690
Carbon Dioxide	0.9	0.6	0.4	0.6	0.6
Oxygen	1.0	1.0	0.4	0.0	0.7
Acetylene	0.5	0.3	0.5	0.3	0.4
Ethylene	1.8	0.9	1.1	1.1	0.6
Aromatics	5.5	2.8	0.3	1.6	1.1
Hydrogen	57.9	46.0	30.9	33.4	36.4
Carbon Monoxide	4.2	10.8	3.4	2.2	2.4
Ethane	0.0	0.0	0.0	0.0	0.0
Methane	22.5	38.5	59.9	60.8	54.6
Nitrogen	5.9	0.0	3.1	0.0	3.2
Total gas cu.ft.	0.7	1.8	3.0	3.3	8.0
Percentage Loss	30.0	30.0	65.0	76.5	81.0
Up to 105°C	0.0	lost	15.0	16.5	11.0
105 to 130°C	5.0	"	13.0	0.0	0.0
130 to 145°C	63.0	"	0.0	0.0	0.0
Above 145°C	2.0	3.0	7.0	7.0	8.0





This series of runs was made with the temperature of the furnace gradually increasing. In each run four to six grams of water were collected. Molybdenum promotes the decomposition of xylene to methane rather than to hydrogen. If the conditions were favorable it should be a good contact surface for the production of benzene.

After completing the runs over molybdenum the furnace was cooled, under an atmosphere of hydrogen, and the carbon deposition removed. At this time some places in the copper lining had given away thus exposing a few small patches of iron surface.

The following runs were made over metallic cobalt cubes. Three kilos 2 cm.square and 3 kilos 1 cm.square, were placed in a paper tube and inserted into the furnace in the usual manner. The temperature was raised to  $470^{\circ}\text{C}$  and the whole outfit kept under a pressure of 60 pounds of hydrogen for two hours before commencing the runs. Even after this treatment moisture was collected in each run, due, presumably, to the reduction of oxides.

The results are given in Table 13.

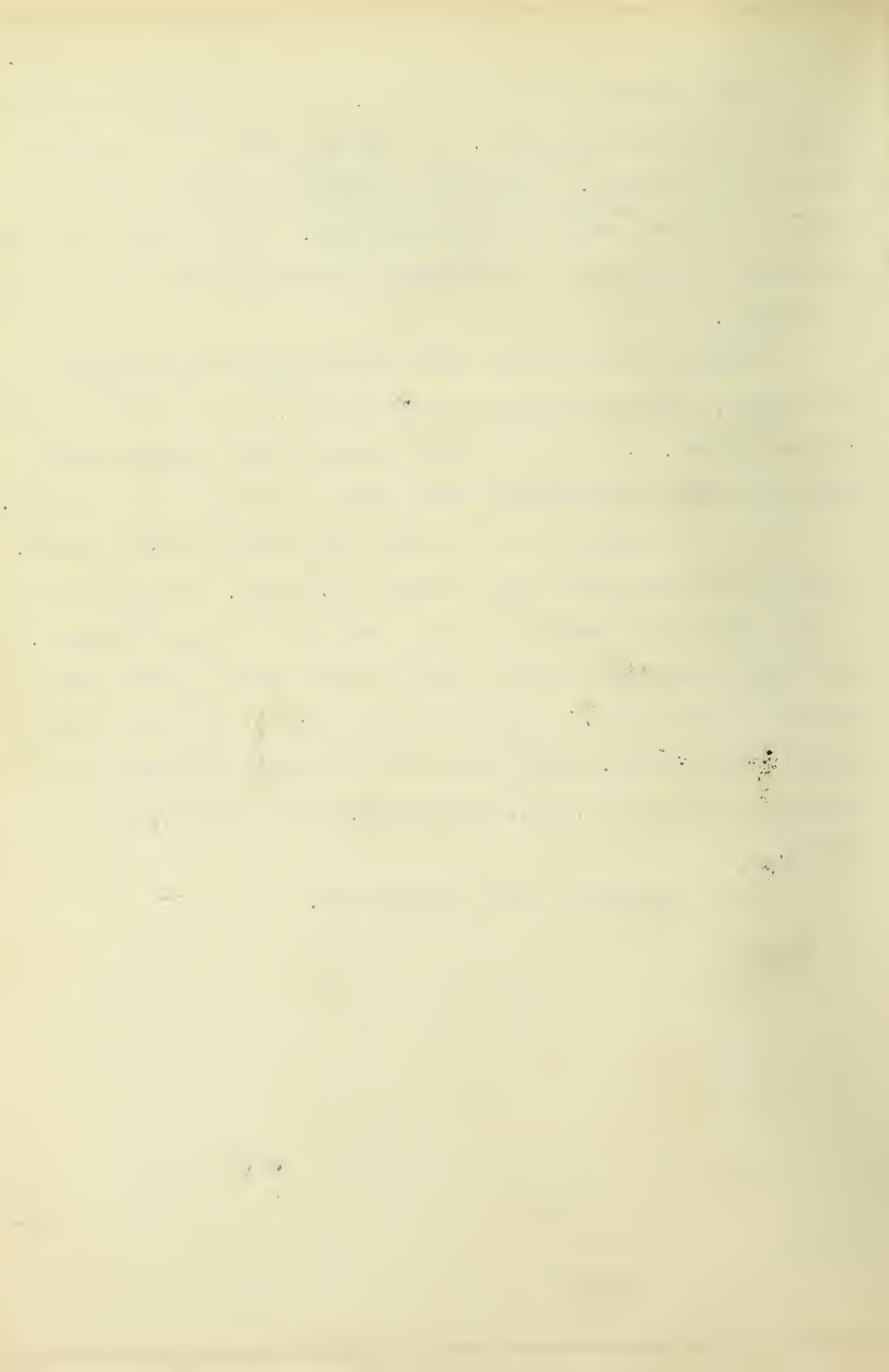


Table 13.

Summary of runs over metallic cobalt cubes. 200 gms. of xylene used per run per hour.

No. of run	140	141	142	143	144	145
Gas introduced	...	...	...	...	...	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	Atm	110
Temperature °C.	475	525	575	625	660	660
Carbon dioxide	0.9	0.7	0.6	0.4	0.5	0.7
Oxygen	0.7	0.1	0.6	1.5	0.6	0.9
Acetylene	0.3	0.6	0.2	0.5	0.4	0.4
Ethylene	1.2	2.4	1.5	1.2	1.4	0.9
Aromatics	0.8	1.2	1.4	1.3	1.3	1.4
Hydrogen	80.2	76.7	76.7	72.8	69.1	32.3
Carbon Monoxide	3.8	4.0	4.6	1.3	0.7	0.4
Ethane	0.0	0.0	0.0	0.0	0.0	0.0
Methane	11.0	12.9	12.6	21.7	26.0	61.4
Nitrogen	1.1	1.4	1.8	0.0	0.0	1.6
Total gas cu.ft.	1.4	2.3	3.2	4.6	5.4	5.1
Percentage loss	35.0	38.0	45.0	73.0	96.5	90.0
Up to 105°C	1.0	tr	2.0	7.5	1.5	8.5
105 to 130°C	4.0	8.0	29.0	12.5	0.0	0.0
130 to 145°C	55.0	50.0	20.5	4.0	0.0	0.0
Above 145°C	5.0	4.0	3.5	3.0	2.0	1.5

The general reactions of cobalt can be seen from the table, however, the influence of some iron surface, although not activated ought not to be underestimated. The tendency to



destroy the hydrocarbon rather than to build it up into higher boiling compounds is evident. Around  $575^{\circ}\text{C}$  cobalt appears to favor the formation of toluene.



Table 14.

Summary of runs, through copper lined furnace over two pounds of finely divided manganese, scattered through small pieces of pumice stone. 200 gms. of xylene used per run per hour.

No. of Run	150	151	152	153	154
Gas introduced	...	...	...	...	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	80
Temperature °C,	565	600	645	685	685
Carbon Dioxide	0.3	0.3	0.5	0.4	0.5
Oxygen	0.4	0.5	0.6	0.2	0.5
Acetylene	0.5	0.5	0.5	0.5	0.4
Ethylene	2.6	3.4	3.1	1.1	1.0
Aromatics	2.1	1.3	0.8	1.7	1.4
Hydrogen	53.4	52.2	42.6	48.8	52.6
Carbon Monoxide	2.9	0.4	0.9	1.2	1.3
Ethane	0.0	0.0	0.0	0.0	0.0
Methane	32.3	40.4	51.0	46.1	39.6
Nitrogen	5.5	1.0	0.0	0.0	2.6
Total gas cu.ft.	1.2	2.1	2.7	4.2	6.0
Percentage Loss	30.0	44.0	50.0	84.0	97.0
Up to 105°C	2.0	4.0	11.0	11.0	3.0
105 to 130°C	24.0	30.0	27.0	0.0	...
130 to 145°C	36.0	6.0	0.0	0.0	...
Above 145°C	8.0	16.0	12.0	5.0	...

This series would indicate that the presence of manganese influences the partial decomposition of xylene at lower





temperatures than the previous metals. In the neighborhood of 600°C the high boiling, as well as the low boiling, products are maximum; also the ethylene content of the escaping gas is highest. Again, the influence of the small, exposed, iron surfaces of the furnace and also the copper lining must be taken into consideration. Some traces of water were noticeable in these runs.

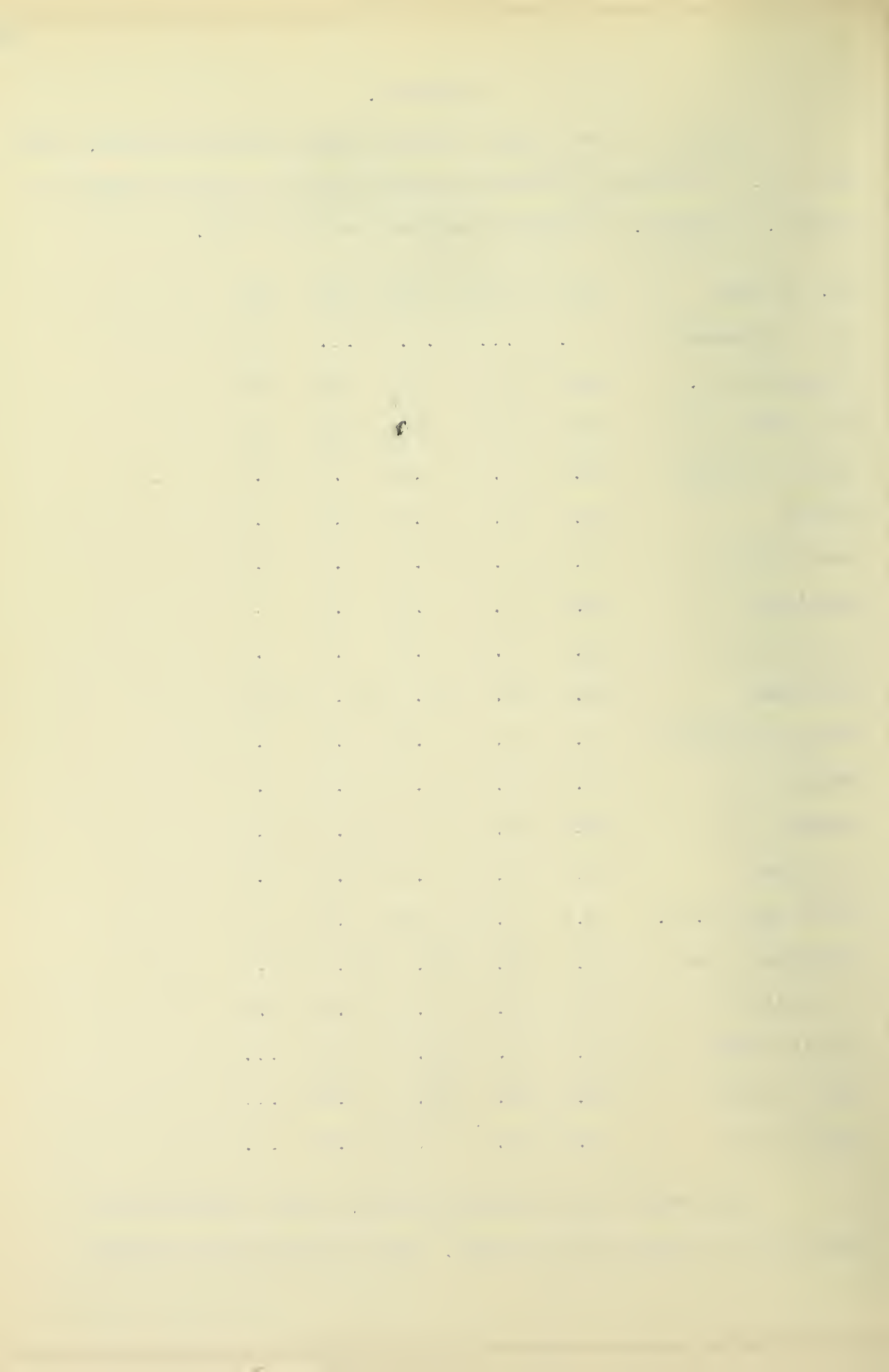


TABLE 15.

Summary of runs made through copper lined furnace, over 440 gms. of aluminum powder scattered through small pieces of pumice. 200 gms. of xylene used per run per hour.

No. of Run	160	161	162	163	165
Gas introduced	...	...	...	...	H <sub>2</sub>
Pressure lbs.	Atm	Atm	Atm	Atm	70
Temperature °C.	525	550	600	680	700
Carbon Dioxide	0.2	0.4	0.6	0.4	0.4
Oxygen	0.1	0.3	0.9	0.7	0.4
Acetylene	0.3	0.3	0.5	0.3	0.2
Ethylene	2.0	2.7	2.0	1.5	1.1
Aromatics	1.8	1.6	1.3	1.0	1.1
Hydrogen	74.0	73.4	76.7	72.5	80.5
Carbon Monoxide	1.6	1.5	0.8	1.0	0.8
Ethane	1.7	0.5	0.0	0.0	0.0
Methane	12.5	16.3	17.2	22.6	15.5
Nitrogen	6.2	3.0	0.0	0.0	0.0
Total gas cu.ft.	0.9	1.5	4.3	5.0	0.4
Percentage Loss	15.0	25.0	65.0	90.0	96.0
Up to 105°C	1.0	0.0	0.0	0.0	4.0
105 to 130°C	8.0	4.0	10.0	8.0	...
130 to 145°C	70.0	67.0	22.0	0.0	...
Above 145°C	6.0	4.0	3.0	2.0	...

Some water was collected in all these runs with the exception of number 163 and 165. When cleaning the furnace



after completing this series the copper lining was found to be broken in so many places, exposing the iron surface, that it was decided to remove it.

#### 10. SERIES OF RUNS USING REFRACTORY LINING IN FURNACE.

The furnace was cleaned by means of a wire brush, heated to  $600^{\circ}\text{C}$  and kept under 100 pounds pressure with hydrogen, for some hours, to reduce any adhering oxide. It was then cooled, under an atmosphere of hydrogen, again cleaned with the wire brush, and then coated by means of a brush, with a thin paste made by mixing 80 per cent of Hytempite with 20 percent Alundum cement. This coating was allowed to air dry before a second coating was put on. The furnace was then heated to  $500^{\circ}\text{C}$  and some runs made to find out the effects on xylene under non-metallic conditions. The results are given in table 16.



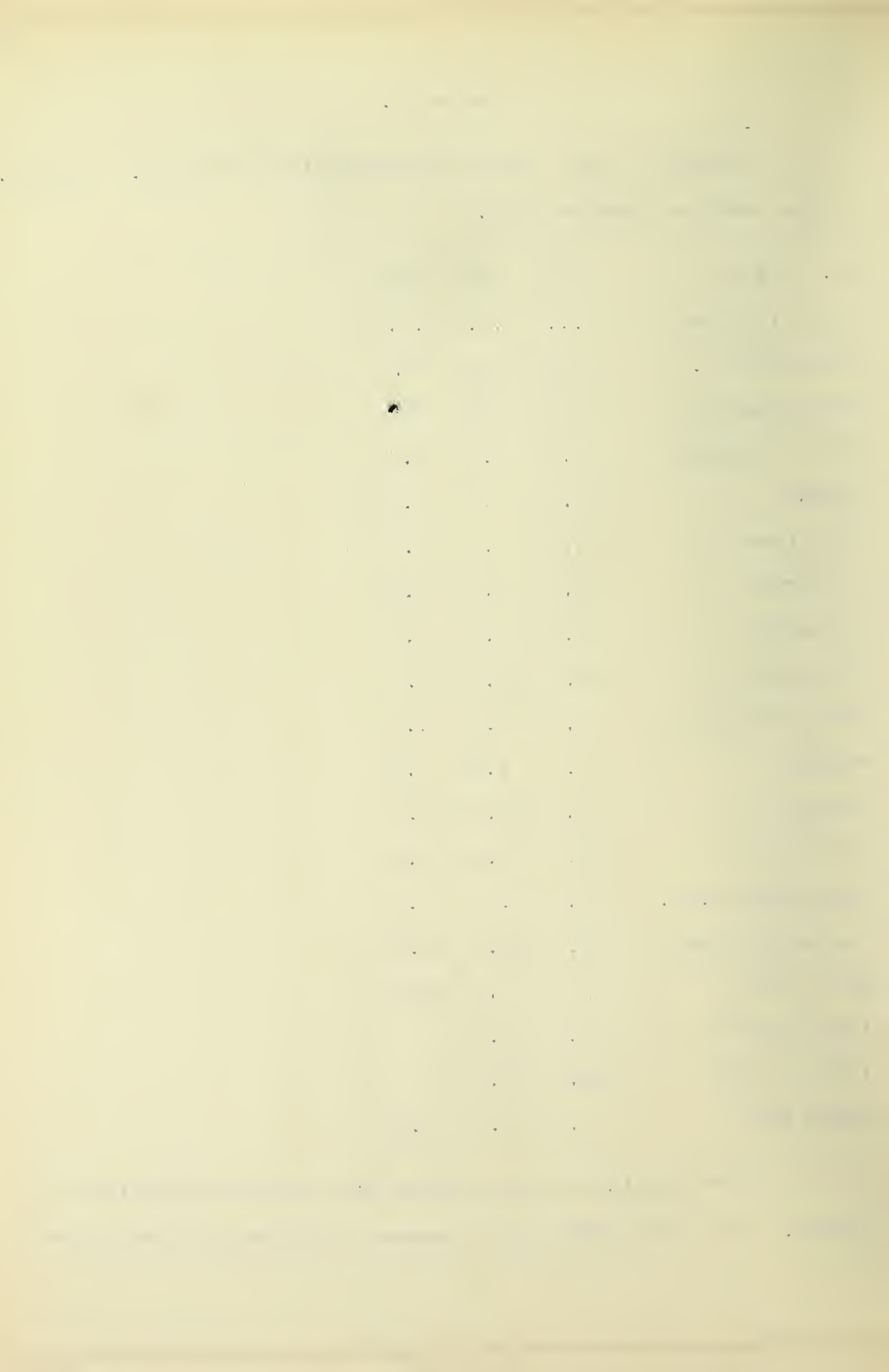


Table 16.

Summary of runs using refractory lined furnace. 200 gms.  
xylene used per run per hour.

No. of Run	166	167	168
Gas Introduced	...	...	...
Pressure lbs.	Atm	Atm	Atm
Temperature °C.	500	550	600
Carbon Dioxide	1.5	0.6	1.0
Oxygen	6.1	5.3	0.4
Acetylene	0.5	0.7	0.6
Ethylene	2.8	4.2	4.4
Aromatics	1.8	4.1	1.8
Hydrogen	55.4	22.1	25.6
Carbon Monoxide	0.6	0.3	2.4
Ethane	0.0	0.0	9.0
Methane	13.0	25.8	42.6
Nitrogen	18.3	36.9	12.2
Total gas cu.ft.	0.2	0.4	1.0
Percentage Loss	25.0	14.0	25.0
Up to 105°C	1.0	1.0	Lost
105 to 130°C	5.0	9.0	"
130 to 145°C	66.0	71.0	"
Above 145°C	3.0	5.0	12.0

After completing this series the furnace was cooled and opened. In a few places small patches of refractory had fallen



off the furnace wall. Directly under these places were found small mounds of carbon, apparently due to the decomposition of xylene by the exposed iron surface.

The furnace was cleaned of all deposited carbon and again coated with the refractory paste. This was to make certain that all iron surfaces were covered before commencing a new series of runs. A cylinder of ethylene, put on the market by The United States Industrial Chemical Co., Curtis Bay, Baltimore, under the trade name of "Calorene" had been secured to use in these runs. In previous experiments it had been noticed, that when the outgoing gas contained any appreciable amount of ethylene, the condensate contained larger amounts of the higher boiling products. In this series the aim was to obtain the maximum percentage of these high boiling compounds. Also to determine, if possible, if by definite control of the atmosphere within the furnace, the desired end products could be obtained. In other words, it was decided that certain definite conditions in regard to temperature and contact surfaces were necessary to practically decompose the xylene molecule, regardless of the end products obtained and, that the reaction could be driven, by mass action, to yield the products desired. That is, if the furnace was in a proper condition to decompose xylene freely, but not too strenuously, that by keeping the atmosphere in the furnace mostly hydrogen, benzene could be obtained as an end product; while if the atmosphere in the furnace was mostly ethylene, the end products would likely be higher boiling compounds.

The results are shown in Table 17.



Table 17.

Summary of runs through refractory-lined furnace, without any other contact surface, using calorene or hydrogen. 200 gms. xylene used per run per hour.

No. of Run	183	184	185	186	187	188	189	190
Gas Introduced	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	H <sub>2</sub>	H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>
Pressure lbs.	45	45	45	Atm	150	125	45	90
Temperature °C.	500	550	600	610	615	650	670	710
Carbon Dioxide	0.0	0.6	0.4	0.4	0.0	0.5	0.3	0.0
Oxygen	0.0	0.4	0.5	0.3	0.1	0.2	0.4	0.0
Acetylene	0.1	0.4	1.0	0.7	0.2	0.3	0.9	0.0
Ethylene	58.4	9.0	3.5	31.1	0.4	0.5	2.6	1.5
Aromatics	0.7	1.3	1.9	0.6	0.4	0.6	1.3	1.2
Hydrogen	2.0	8.6	6.7	4.0	60.0	58.7	6.0	28.8
Carbon Monoxide	3.5	4.9	3.3	3.1	4.0	5.2	4.4	6.8
Ethane	12.7	7.4	8.6	22.8	0.0	0.0	0.0	0.0
Methane	23.0	67.4	73.3	37.0	34.9	35.7	84.1	62.3
Nitrogen	0.0	0.0	0.7	0.0	0.0	0.0	0.0	0.0
Total gas cu.ft.	1.3	0.8	0.5	10.0	6.5	7.4	0.4	4.3
Percentage Loss	+1.0	22.0	34.0	<sup>22.3?</sup> <del>27.0</del>	26.0	37.5	75.0	67.5
Up to 105°C	tr.	7.5	18.5	tr	69.0	55.5	10.0	17.0
105 to 130°C	3.0	24.0	4.0	0.0	0.0	0.0	0.0	0.0
130 to 145°C	79.0	16.5	0.0	0.0	0.0	0.0	0.0	0.0
Above 145°C	18.0	30.0	43.5	77.7	5.0	7.0	15.0	15.5

The first runs of this series were made at 350, 400, 415, 450 and 475°C. They were all made under a pressure of 45 pounds





built up by ethylene from the cylinder. At these temperatures there was very little decomposition of xylene, ranging from two to eight percent, the majority going into higher boiling compounds. In each of these runs, however, there was a gain in weight, from one-half to one and one-half per cent of the original xylene. This was found to be due to dissolved ethylene, which was driven off again when fractionating the condensate. Another significant result shown by the gas analysis was the stability of ethylene under these conditions. At  $415^{\circ}\text{C}$  the waste gas contained 89.4 percent ethylene, no ethane and 8.5 percent methane; while at  $475^{\circ}\text{C}$  it contained 73.9 percent ethylene, 4.6 percent ethane and 8.0 percent methane. At  $500^{\circ}\text{C}$  the maximum percentage of ethane was obtained while the percentage of methane increased with temperature.

In all the runs with ethylene, it was necessary to conserve the gas as much as possible, so that, when running under 45 pounds pressure, the waste gas was allowed to escape slowly, otherwise no ethylene could be added because the decomposition gas kept the pressure increasing. Run 184 indicated that the conditions, where all the xylenes were being decomposed were being approached. Run 185 showed the optimum temperature was in that neighborhood, also that the conditions were favorable for the formation of high boiling compounds. At this temperature ethylene was found to decompose rapidly the majority going to methane. Now for the building up of high boiling compounds the larger the excess of ethylene in the furnace the better,

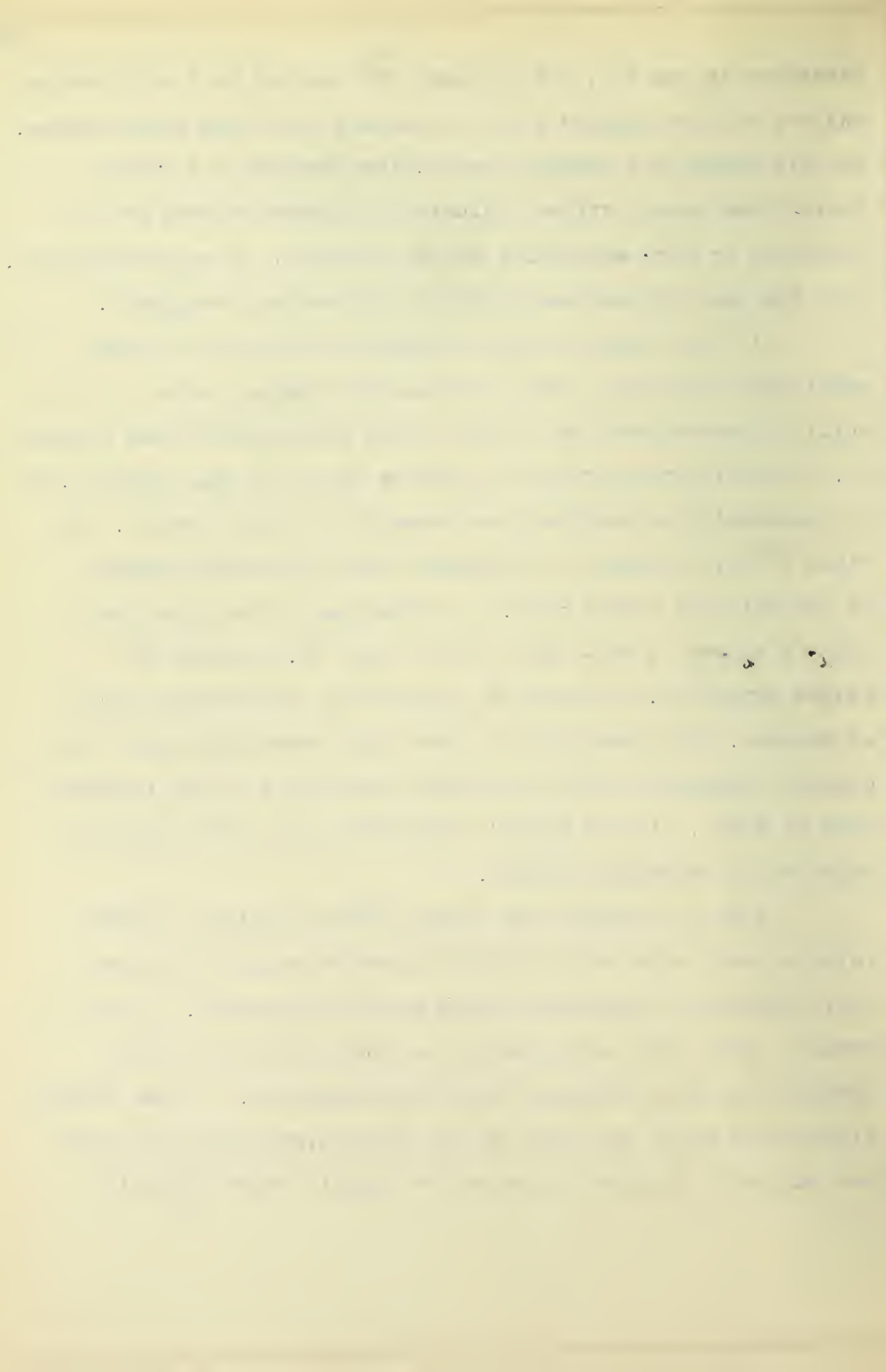




therefore in run 186, the pressure was reduced to 4 or 5 pounds, and the ethylene passed into the furnace in a very rapid stream. In this manner the products were driven through the furnace faster than usual, without allowing the decomposition of the products, or more especially of the ethylene, to become complete. This run gave the maximum yield of high boiling compounds.

At this point it was desirable to find out if these particular conditions were favorable for forming lower boiling hydrocarbons and if they could be stabilized and recovered. Run 187 gave conclusive evidence that this was possible. It is interesting to analyze these results a little farther. The yield of 69.0 percent is calculated from the weight percent of the original xylene used. By referring to the equation,  $C_8H_{10} + 2 H_2 \rightleftharpoons 2 CH_4 + C_6H_6$  we see that 69.0 percent by weight equals 93.8 percent of the possible theoretical yield of benzene. The remainder of these runs demonstrate that the optimum temperature for the desired results is in the neighborhood of 600°C. At the higher temperatures the water collected appeared to increase slightly.

When the furnace was opened, after cooling, the whole interior was coated with a fluffy layer of carbon, which was very different in appearance from previous deposits. It was a metallic gray color and granular or sandy, while the other deposits had been intensely black and amorphous. It was evenly distributed along the walls of the furnace, even where no iron was exposed. In previous cases the deposits were directly



opposite the exposed iron surfaces. It does not seem possible, that the very small amount of iron exposed could have been responsible for all the carbon deposited, however, it may have started the reactions which were carried along by the carbon thus deposited.

The next series of runs, after cleaning the furnace entirely free from carbon, were made with some small patches of iron exposed. This was calculated to promote the decomposition of xylene at lowered temperatures and thus allow a better yield of high boiling compounds. Table 18 shows that this was only partially successful.



Table 18.

Summary of runs through refractory lined furnace with some iron surface exposed. 200 gms. of xylene used per run, the time of feed varied from 5 minutes to four hours.

No. of Run	200	203	205	207	208	210	211	212
Gas Introduced	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	Steam	Steam C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>
Pressure lbs.	45	125	140	60	Atm	Atm	145	75
Temperature °C.	525	490	580	620	615	585	525	460
Carbon Dioxide	1.1	0.4	0.0	0.0	0.6	1.4	0.6	not
Oxygen	0.2	1.8	0.3	0.2	0.5	0.5	1.7	run
Acetylene	0.5	0.7	0.3	0.3	0.5	0.5	0.5	
Ethylene	21.8	25.1	5.1	1.6	6.2	33.0	13.0	
Aromatics	1.0	0.6	0.8	0.3	0.5	0.6	0.0	
Hydrogen	13.4	7.2	6.6	39.5	43.3	30.9	2.0	
Carbon Monoxide	4.2	3.1	2.3	2.6	1.6	1.1	4.5	
Ethane	30.9	21.9	8.3	8.0	0.0	0.0	15.1	
Methane	26.9	33.0	75.3	47.5	45.6	32.0	60.4	
Nitrogen	0.0	6.2	1.0	0.0	0.2	0.0	2.2	
Total Gas cu.ft.	2.5	2.4	5.2	14.6	2.4	3.1	12.2	12.5
Percentage Loss	20.0	9.0	25.0	87.5	24.0	30.0	75.0	27.5
Up to 105°C	1.5	1.0	6.0	12.5	tr	tr	Lost	20.0
105 to 130°C	10.0	10.0	20.0	....	25.0	20.0	"	4.0
130 to 145°C	53.5	22.0	14.0	....	44.0	40.0	"	41.0
Above 145°C	15.0	58.0	35.0	tr.	7.0	10.0	7.5	7.5

These runs were made under what might be termed extreme conditions, to find out if any favorable condition such as pressure duration of time of contact and mass-action equilibrium had been neglected in previous runs.







Run 200 was fed at the rate of one drop per second. This was to allow ample time for equilibrium to be obtained among the gases in the furnace. The decomposition was not excessive but the most interesting feature brought out is the percentages of ethylene, hydrogen, ethane and methane in the issuing gases. In run 201 the 200 gms. of xylene was fed in ten minutes. Here the recovered products were of equal weight to the xylene used. The ethylene was fed in an atmospheric pressure and quite rapidly. Only 40 percent of the xylene used was changed, it going almost equally into high and low boiling compounds. In run 202 the xylene was fed intermittently, while the ethylene was fed continuously at atmospheric pressure. A marked increase in the high boiling constituents was noticeable. In run 203 the feed interval was about thirty minutes. This contact period seemed favorable for building up the high compounds. In run 211 the rate of feed was 80 drops of xylene per minute; while in all the other runs the former feed rate of 200 grams per hour was used. In runs 206 and 207 the furnace became activated in such a manner, that regardless of how fast or under what pressure ethylene was added, all the hydrocarbons were decomposed to gas and deposited carbon. In fact, it was very similar to the previously mentioned activated conditions. The introduction of superheated steam caused similar effects as previously. The experiments with xylene were discontinued after run 213. When the furnace was opened the deposited carbon had a very peculiar formation. It was suspended from the top of the furnace in ~~long~~ fibres from one to two inches long.



They might be said to resemble in shape, delicate stalactites.

The large increase in the yield of the high boiling hydrocarbons, obtained in the last two series of runs, made it seem profitable to fractionate them further. The results are given in Table 19.



Table 19.

Fractionation of high boiling products obtained from the decomposition of xylene. The percentages given in (A) were obtained on 165 grams of high boiling product obtained in the series of runs tabulated in table 17. The results given in (B) are from 325° of high boiling product obtained from the series last tabulated.

Boiling range	A	B	Sp.Gr. .15.5°C.	Remarks
145 to 175°C.	11.5	6.6	0.8911	Light greenish oil
175 to 200°C.	....	8.9	0.9057	Light oil, at zero-solid
200 to 225°C.	23.1	4.8	0.9605	Darker oil, at zero-solid
225 to 240°C.	5.8	7.2	0.9888	" " " " "
240 to 255°C.	12.7	8.3	1.0087	High oil with white "
255 to 300°C.	8.0	15.1	1.0282	Oil - shade darker
300 to 350°C.	19.3	23.4	1.0625	" " "
350 to 400°C.	8.0	14.5	1.1082	Reddish oil with yellow solid
400 to 500°C.	7.0	7.1	Solid	" yellow solid
500 to coke	4.5	4.0	"	Tar.
Crude oil.			1.0808	

These results show, that in the last series where greater pressures were used, the higher boiling products contained a larger percentage of solids. In each of these series the final residue or coke amounted to about 4% of the high boiling product.





## 11. SERIES OF RUNS USING BENZENE.

The runs on benzene were made through the iron furnace containing  $2\frac{1}{2}$  kilos of charcoal. The purpose being to try to check Cobb and Hollings<sup>23</sup> results. They found that benzene, while passing through coke heated to  $800^{\circ}\text{C}$  could be entirely stabilized by means of excess hydrogen. In these experiments it was found that when the charcoal and furnace was activated, that it was impossible to stabilize the benzene even at  $500^{\circ}\text{C}$ . Pressures as high as 125 pounds of hydrogen per square inch were used. On the other hand, if the charcoal and furnace had been treated with superheated-steam, air or carbon dioxide, that the benzene could be entirely stabilized at temperatures as high as  $800^{\circ}\text{C}$  with a very small pressure of hydrogen. The condensation products, other than recovered benzene were not analysed.

## 12. SERIES OF RUNS USING TOLUENE.

Cobb and Hollings had found, that when toluene was passed through red hot coke, that it was more stable alone than when in the presence of hydrogen. That is, hydrogen caused the decomposition of toluene to benzene and methane. In run 58, Table 4, hydrogen was found to increase slightly the toluene fraction. Pure toluene was run under similar conditions and it was found that toluene was somewhat more stable in the presence of hydrogen. In cases where the furnace was activated the toluene was entirely destroyed with or without hydrogen.





### 13. SERIES OF RUNS USING NAPHTHALENE.

In making the runs on naphthalene, it was preheated in an electrical retort, connected to the top end of the furnace and the vapors carried into the furnace by means of the gasses bubbled through. The products obtained have not all been identified but the analysis of escaping gas is interesting.



Table 20.

Summary of runs over  $2\frac{1}{2}$  kilos of charcoal in iron furnace, with preheated naphthalene, carried into the furnace by means of gases. 300 gms. of naphthalene used per run, at atmospheric pressure.

No. of Run	220	221	222	223	224	225
Carrier gas.	CO <sub>2</sub>	CO	CO	H <sub>2</sub>	N <sub>2</sub>	CO <sub>2</sub>
Pre-heat Temperature°C.	340	320	340	330	330	325
Furnace Temperature°C.	780	525	635	660	640	815
Gas used cu.ft.	2.6	2.4	3.5	3.2	1.4	2.0
Gas recovered cu.ft.	2.6	0.4	2.6	1.4	0.9	1.7
Percentage loss	+0.5	67.5	22.0	28.0	33.3	65.0
Carbon dioxide	36.0	17.7	34.8	2.9	1.2	2.8
Oxygen	4.4	5.2	2.0	2.6	0.8	1.6
Acetylene	0.2	0.3	0.5	0.4	0.1	0.3
Ethylene	0.0	0.0	0.3	1.0	0.2	0.4
Aromatics	0.1	0.0	0.3	0.0	0.1	0.4
Hydrogen	34.8	38.2	21.6	85.1	6.1	72.0
Carbon Monoxide	14.8	17.3	35.6	1.4	2.2	22.5
Ethane	3.0	2.8	1.8	0.4	0.2	0.0
Methane	5.5	0.2	0.2	0.6	0.3	tr
Nitrogen.	2.2	18.3	2.6	5.6	88.8	0.0

In the runs on naphthalene it was noticed that practically as soon as the run commenced the temperature of the furnace dropped. Even when the current passing through the heating elements, was materially increased, the temperature fell slowly.



This would indicate the reactions taking place inside the furnace was absorbing considerable heat. Another feature, particularly noticeable in the nitrogen run, was that the gas recovered did not equal the amount passed into the furnace from the cylinder, even with the addition of the gas from decomposition of the naphthalene. The charcoal may be partly responsible for this result.

In the runs using carbon dioxide as the carrying gas, the product contained a heavy, black, high boiling oil, some free carbon, and a very light, fluffy, red material with very little odor of naphthalene. With hydrogen the product was dark gray containing also traces of the light reddish material. The product from the nitrogen runs was a compact greenish color and from carbon monoxide the reddish fluffy material formed the bulk of the recovery.

### III. SOME PRODUCTS SYNTHESISED IN THE INVESTIGATION.

A few of the products, obtained in this investigation, require rather strenuous mental gymnastics to explain their formation. From the kinetic theory, the intermolecular collisions, which increase with rise in temperature, would account for the rupture of bonds or forces which hold together atoms or groups. Also under like conditions the larger molecules, - higher boiling compounds, - would have a greater momentum than the smaller ones, and on this account at the instant of impact, would be subjected to greater strain. That is, at higher temperatures, benzene should be more stable than toluene or xylene; or to obtain toluene from xylene lower temperatures would be more favorable.





The process of decomposition of hydrocarbons can never be regarded as a simple effect of heat independent of the gaseous atmosphere in which it is conducted and the way in which we hope to modify the results of decomposition in various directions is by the deliberate control of that atmosphere. The gaseous products obtained in these experiments are extremely important and play as important a part in the final products as the gas introduced. Their effects can be considered from two standpoints, mechanical and chemical. An inert-gas, like nitrogen, would not enter directly into chemical reaction under these conditions, but would play a very important part by washing the products of decomposition from the surface of the contact material, assist their volatilization by lowering their concentration in the vapor phase, and hurry them away from the region of decomposition. In the case of hydrogen, being much lighter, it has a greater diffusing power, the molecules travel at a higher speed and thus penetrate small areas where the larger gas molecules never reach. The all-important action of hydrogen, however, is chemical. It tends to reduce the single ring benzene compounds to benzene itself. A similar action may be inferred, as is very probable, on the attached groups of more complicated ring compounds, resulting in the formation of naphthalene and anthracene. It seems that this was the part played by hydrogen in the majority of the experiments carried out. However, other factors must be able to modify this tendency of hydrogen because in the experiments giving the largest yields of the toluene fraction, it was found possible to increase this fraction by introducing hydrogen from a cylinder, although it was not definitely proven that this increase was not



due to benzene.

It was possible to change the production of hydrogen in these experiments by changing the temperature, or the activity of the furnace.

Methane could also be produced in varying quantities, depending upon the furnace conditions. Bone and Coward<sup>24</sup> concluded that methane decomposes chiefly, directly into hydrogen and carbon, the process being reversible and a surface phenomenon at least up to 1200°C. At the temperature these experiments were run, methane is practically stable and its chemical reaction would be negligible but its mechanical action would be very important as in the case of nitrogen.

The carbon dioxide formed was in small quantities and was always in equilibrium with carbon monoxide. They seemed to deaden or poison the activity of the furnace, although it is possible they caused partial combustion.

Acetylene was formed in small quantities and although many investigators claim that the building up process is through the ability of acetylene to polymerize, it was concluded from these experiments, that acetylene played a very small part. At higher temperatures, it was more liable to be decomposed to carbon and hydrogen than to be built up.

The production of ethylene in these experiments was very desirable, because, it was noticed that wherever the percentage of ethylene in the outgoing gas, was around three or four percent, the yields of the higher boiling compounds were appreciably increased. In general, it was found, that ethylene decomposed





into a mixture of ethane and methane in the neighborhood of  $500^{\circ}\text{C}$ . Above  $500^{\circ}\text{C}$  the ethane content gradually decreased and around  $650^{\circ}\text{C}$  disappeared entirely with a resultant increase in methane. Ethylene seems to be able to decompose in several ways, which no doubt explains its usefulness in the building up process.

Bone and Coward concluded that the primary action of heat on ethylene is to eliminate hydrogen. The residue  $:\text{CH}$  thus formed may decompose or be hydrogenated to methane, or it may unite with another such residue to form acetylene. Hollings & Cobb found that at lower temperatures, around  $800^{\circ}\text{C}$  it decomposed into methane and acetylene, while at higher temperatures it went into methane and hydrogen.

In some of these experiments as high as 15% of the waste gas was found to be ethane. It was also found that very little ethane was formed below  $600^{\circ}\text{C}$  and that it was all practically decomposed at  $700$  to  $725^{\circ}\text{C}$ , except in the presence of steam, which seemed to stabilize it at slightly higher temperatures. These temperatures are far lower than found by Hollings and Cobb who found that the decomposition of ethane was rapid, but not complete in 46 seconds at  $800^{\circ}\text{C}$ . At  $1100^{\circ}\text{C}$  only 88 percent was decomposed, the chief products being ethylene and methane. No doubt the molecular decomposition of ethane played an important part in these experiments. According to J.J. Thomson<sup>25</sup>, such residues as  $:\text{CH}$ ,  $:\text{CH}_2$  and  $\cdot\text{CH}_3$  may exist momentarily in the free state. The four possibilities open to the residue  $:\text{CH}_2$  are: (1) to form ethylene by contact with another similar residue; (2) to break down into carbon and hydrogen; (3) to be hydrogenated to methane;



(4) or attach to some heavier molecular formation, - a partial decomposition, of the benzene nucleus or homologues.

The above is only a partial list of the gaseous constituents in the furnace atmosphere during decomposition, undoubtedly many more complex groups or radicles from the higher boiling compounds exerted an important influence on the process.

A few of the liquid hydrocarbons obtained in this investigation are listed below. All were definitely identified by the common tests and known derivatives were made. These results are qualitative only, as no definite scheme of separation has been worked out. Mr. Malecki is working on the solid and liquid products obtained in this investigation, and his methods of separation, purification and identification will be given in his graduation thesis in February 1922.

N-Hexane (B.P.68) was obtained in very small quantities along with another highly unsaturated hydrocarbon, which boiled around the same temperature, in the runs made under high pressure with ethylene.

Cyclo hexane (B.P.80) was also obtained in very small quantities in the same runs.

Benzene (B.P.80.5) was recovered and purified from several runs. The largest yield of the crude product obtained was approximately 93.0 percent of the possible theoretical.

Toluene (B.P. 110) was obtained in many of the runs over charcoal. The maximum yield of the crude product being about 66.0 percent theoretical. Very little work has been done on the higher





boiling compounds listed in table 19, Only three having been definitely identified.

Ditolyls (mixed, B.P. about 275C) were identified.

A-Methylnaphthalene (B.P.240-242) has also been purified; while diphenylethane (B.P.286) has been obtained in small amounts.

The solids synthesised in this investigation are also extremely complex. In a single series of runs the high boiling constituents were very similar in each run, but in different series the variation was marked. It was quite noticeable that when using cobalt and manganese, the high boiling oils had a larger percentage of solids containing anthracene. Only a very few of these solid compounds have been purified. A partial list follows:

Diphenyl (M.P.70°) was obtained in considerable quantities in the fraction boiling from 240-255°C. On standing it settled out as a white solid. This product would come from two benzene molecules with the liberation of hydrogen. Durfton and Cobb have proven this to be a reversible reaction by passing diphenyl and hydrogen through a hot silica tube and producing benzene.

Napthalene (M.P.80°) was obtained in considerable quantities, as closely as could be determined, in approximately 4% yields on the original xylene used. In view of the conflicting reports in the literature concerning the formation of napthalene at low temperature and from similar liquids, toluene especially, particular care was taken in the identification of this compound. The presence of stilbene may give a clue to its formation.



Stilbene (M.P.  $124^{\circ}$ ) was found in very small quantities, apparently it had been mostly condensed to naphthalene.

Methyl Anthracene (M.P. 198-200) mixtures of the A and B compounds have been obtained.

P-Diphenyl Benzene (M.P. 207) has also been identified.

Anthracene (M.P. 214-216) has been purified.

2.3 Dimethyl-Anthracene has been purified, and the other forms are also present, but so far have not been purified. A mixed quantity of trimethyl anthracene is also present.

Chrysene (M.P. 248-50) was obtained in small amounts in the runs, with ethylene and xylene, under high pressures.

Another compound which has been separated, is very similar to asphaltenes in its appearance, behavior toward solvents, especially ether and hexane, and contains sulphur. It is not easy to determine where the sulfur came from to enter the reaction, unless it was obtained from the charcoal, metals or pumice stone.

No doubt many more compounds may be identified but the above list is sufficient to demonstrate the extremely complex molecular formations which were produced in these experiments.

It is evident that any compound that can be synthesised from benzene or toluene by pyrogenetic decomposition, under similar conditions to the above, can also be produced from xylene, because it is capable of being broken down into similar groups or atoms or molecular formations.





#### IV. SUMMARY

Some of the most important facts established by the foregoing investigation are given in the following summary.

(1) Mixed xylenes, under favorable conditions of temperature, contact surfaces and pressure, can be decomposed into toluene or benzene. The gaseous atmosphere most favorable to this reaction is either methane or hydrogen.

(2) Under identical conditions of temperature, contact surfaces and pressure, xylenes can be built up to form naphthalene, anthracene, and the methyl derivatives of both. The gaseous atmosphere favoring the reaction is preferably ethylene or other unsaturated gaseous hydrocarbons.

(3) Metallic Oxide surfaces, especially after being slightly reduced at temperatures where they decompose xylene freely, influence to complete decomposition of the hydrocarbons to hydrogen, methane and carbon.

(4) The reduced metallic surfaces, or freshly oxidized surfaces at the same temperature is much less reactive, and influences to partial decomposition.

(5) Non-metallic substances such as charcoal, pumice, or refractory material at like temperatures tend to decompose xylenes into unsaturated and higher boiling compounds. The decomposition to carbon is materially lessened.

(6) The gaseous atmosphere in which pyrogenic decomposition takes place exerts an extremely important influence on the products of decomposition. Gases like methane and nitrogen between





temperatures of 600 to 700°C have only a mechanical action.

Ethylene, acetylene, hydrogen and ethane between the same temperatures have also a mechanical bearing on the end products. Their all-important action, however, is chemical, tending to produce high-boiling compounds; ethylene, acetylene and ethane were found to be entirely decomposed at temperatures above 725°C.

(7) By the deliberate control of the gaseous atmosphere under which decomposition takes place, the yields of the desired products can be greatly increased.

(8) Steam, air and carbon dioxide poison or deaden activated surfaces, in such a way that they appear to stabilize liquid hydrocarbons.

(9) Contact surfaces are very important in hydrogenation and dehydrogenation of aromatic hydrocarbons.

(10) Pressure under some conditions favors molecular condensation that is, if the pressure is made up of unsaturated gases. In other cases it caused, where the pressure was made up by hydrogen, the decomposition of the heavier molecules into the single ring compounds. Pressure in all cases lessened the percentage of unsaturated hydrocarbons in the final products.

(11) Decomposition of hydrocarbons increases with rise in temperature. The larger molecules being less stable than the smaller ones at temperatures above 700°C. The lower the temperature at which decomposition takes place the more economical the reaction. Lower temperatures can be used in the presence of activated surfaces.

(12) Practically all of these reactions are reversible.



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## VI. VITA

The writer of this thesis received his early education in the grade school at Leskard, and high school at Bowmanville, Ontario, Canada. He graduated from McMaster University, Toronto, in June 1915, with the degree of Bachelor of Arts, in the honor science course. In September, of that year, he received the degree of Master of Science from the same University.

After graduation he entered war munition work. From Sept. 1915 to March 1916 analysing high explosives at the plant of The Canadian Explosives Ltd., Montreal. From March 1916 to November of the same year analysing 9.2 inch sheel steel, at the plant of The Canada Cement Co., Montreal. During November he was at the plant of The Armstrong-Whithworth Co., Longuiel, Quebec, analysing tool steel. From December 1916 to October 1917 he was with The British Munitions Board, stationed at the acetone plant, of The Canadian Electro Products Co., Shawinigan Falls, Quebec.

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